

# COMPARISON OF SEVERAL EXTRACTANTS FOR AVAILABLE PHOSPHORUS AND POTASSIUM

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## INTRODUCTION

Selection of a soil test extractant is contingent upon its ability to extract nutrients which are well correlated with plant response. The sodium bicarbonate method (Olsen et al., 1954) currently in use at the University of Saskatchewan Soil Testing Laboratory for the evaluation of available P and K could achieve this purpose (Halstead, 1969 and Rennie et al., 1966). The sodium bicarbonate was considered as a suitable extractant to evaluate the availability index of P especially in neutral, alkaline and calcareous soils (Olsen et al., 1954 and Shi, 1980). This method, however, possesses some disadvantages. The first shortcoming is the relative inconvenience and time-consuming process of driving off CO<sub>2</sub> from the extract and the difficulty of obtaining proper pH during acidification prior to P colorimetric measurement. The second problem is from the activated carbon used. It is difficult to obtain P-free activated carbon and the use of it could cause staining of laboratory ware and technicians clothing. Besides, long shaking time lowers production.

Researchers have been much interested in developing multi-element extractants (Baker, 1971; 1973, Mehlich, 1978b; Soltanpour et al., 1977 and van Lierop, 1988) to save labor and supplies for routine soil testing. The Saskatchewan Soil Testing Laboratory usually receives 25,000 farm field samples per annum for routine macro-nutrient testing in which nearly 800 samples are also used for micro-nutrient analysis. In considering the large ratio of 31 to 1, a new extractant with the potential only for simultaneous extraction of N, P, K and S is an attractive option. Sodium bicarbonate itself could be considered as a choice; but the use of activated carbon causes high NO<sub>3</sub><sup>-</sup> contamination. NO<sub>3</sub><sup>-</sup> free activated carbon can be obtained by the rinse of deionized water before use. Unfortunately, the pre-treatment of activated carbon would add too much time and extra costs to achieve. Hence, sodium bicarbonate cannot be considered as a "candidate" for quadruple-element extractant in routine analysis.

In this study, our attempt is to adopt or develop an improved extractant for P and K determination over a wide range of soil conditions as the replacement of sodium bicarbonate presently used in this laboratory. Of course, it appears that the new test solution must have a potential to simultaneously extract N, P, K and S. To that end, three extractants named as Kelowna (Ke), modified Kelowna (KM) and modified Bray/Kurtz (BM) were compared with the Olsen extractant and were evaluated for their suitability as a substitute of the Olsen in routine soil testing analysis.

## MATERIALS AND METHODS

### Soils

The soil samples used in this study were submitted by farmers for routine analysis in 1989. These soil samples were air-dried, ground and screened through a 2-mm sieve. After the completion of routine analysis for farmers, a total of 400 samples from 0 - 15 cm depth were selected to represent a wide range of soil test values and other soil properties from all six soil zones in Saskatchewan. The texture of soils used included sand, loam, clay and their transitive types. The soil pH and EC in 1:1 of soil:water suspension were

between 5.4 and 8.4. and 0.1 to 3.5 mS cm<sup>-1</sup>, respectively. The sodium bicarbonate extractable P and K of the soils studied ranged from 3.3 to 50 µg g<sup>-1</sup> and from 43 to 827 µg g<sup>-1</sup>, respectively. The soil nitrate in 0.001M CaCl<sub>2</sub> (1:2) were between 0.7 and 57.8 µg g<sup>-1</sup>.

### Extractants

The three extractants used in this study for the comparison with the Olsen extraction were as follows:

**Kelowna Extractant (Ke):** The Kelowna extracting solution consists of 0.25N HOAc and 0.015N NH<sub>4</sub>F with a measured pH value of 3.2. It is a multi-element extracting solution which was first used in British Columbia in 1984 to simultaneously extract P, K, Ca, Mg, Na, S and NO<sub>3</sub> from acid and calcareous soils (van Lierop, 1988). Ke can exhibit buffering during the extraction. Its buffer action is produced by the addition of a base like calcium carbonate while extracting. Therefore, Ke performs in calcareous soils as well as in non-calcareous soils for the extraction of P (van Lierop, 1988). It is well known that plant roots excrete organic acids. As an organic acid, acetic acid provides a similar rhizosphere circumstances (Shi, 1980). Ke seems to be a hopeful replacement for available P and K determination to achieve a positive plant response in Saskatchewan soils.

**Modified Kelowna Extractant (KM):** The neutral 1.0 N NH<sub>4</sub>OAc solution is known as a standard extractant for evaluation availability index of K (Knudsen, 1982 and Shi, 1980). Ke was reported to extract about 20% less K than standard NH<sub>4</sub>OAc (van Lierop and Gough, 1988). While simultaneously extracting P and K, the combination of a diluted NH<sub>4</sub>OAc solution with Ke may improve the extraction of K without any new ionic species added in it. The KM will consist of 0.25 N HOAc and 0.015 N NH<sub>4</sub>F as well as 0.25 N NH<sub>4</sub>OAc with a measured pH of 4.9. HOAc and NH<sub>4</sub>OAc reactant has been reported to give a good prediction for available S (Islam, 1988 and Yli-Halla, 1987). Considering a further study on its simultaneous extraction for N, P, K and S, KM may have the potential to achieve a satisfactory indication of each of the four macro-nutrients.

**3, Modified Bray/Kurtz Extractant (BM):** The Bray/Kurtz extractant consists of 0.025 N HCl and 0.03 N NH<sub>4</sub>F. This mild acid solution test has been well correlated with plant response from acidic to neutral soils (McLean et al., 1979 and Vanghn, 1980). The reaction in calcareous soils, however, has showed less effective due to the formation of CaF (Mehlich, 1978a and Smillie et al., 1972). This problem could be overcome by widening the soil/extractant ratio to 1:50 (Randall et al., 1966 and Smith et al., 1957). A soil:water ratio of 1:50 is a very wide ratio. It does extract larger amounts of P but the concentration of P is lower. In order to meet both extraction effectiveness and suitable concentration in extract, a 1:25 of soil:extractant ratio was used in this study. The purpose of a chemical test for plant nutrients is to obtain a predictable plant response. It does not mean that all the available P must be extracted. It is not true that the larger soil:extractant ratio used, the better the results obtained (Shi, 1980).

The Bray / Kurtz extractant was originally designed for P, but it was also reported to be used for K measurement (Peterson et al., 1971) Based on cation exchange, nevertheless, any NH<sub>4</sub>-containing solution can be considered a suitable extractant for exchangeable K. Introduction of diluted NH<sub>4</sub>Cl solution to Bray / Kurtz will not produce any new ionic species.

### Extraction Procedures

The extraction procedures followed are summarized in Table 1.

All soil samples were extracted in triplicate for each extraction. A control soil sample was also extracted with each extraction. After extraction, the soil extracts were filtered using Whatman No. 42 paper. A portion of the filtrate was transferred to

Technicon Auto Analyzer sampling cups for the determination of P and K. A reagent blank and a control sample filtrate were also included with each set of 48 samples. In the automated system, the extractable P and K contents were determined by colorimetry using ammonium molybdate and ascorbic acid and by flame photometry, respectively.

Table 1. Chemical composition and procedure used in the extraction of P and K by the four different methods studies

Methods	Solution Composition	Solution pH	Soil : Solution	Shaking Time (min)
Ke	0.25N HOAc+ 0.015N NH <sub>4</sub> F	3.2	1 : 10	5
KM	0.25N HOAc + 0.015N NH <sub>4</sub> F + 0.25N NH <sub>4</sub> OAC	4.9	1 : 10	5
BM	0.25N HCl + 0.03N NH <sub>4</sub> F + 0.1N NH <sub>4</sub> Cl	2.5	1 : 25	1
Olsen	0.5N NaHCO <sub>3</sub>	8.5	1 : 20	30

Finally, correlation and linear regression analyses were performed to compare P and K values determined by three different extractants with those extracted by the Olsen method.

## RESULTS AND DISCUSSION

The results from the control sample analysis showed that all three extractants studied can provide lower day to day laboratory variability than Olsen (Table 2 ).

Table 2. Control Soil Sample Statistics.

Nutrient	Extractant	Mean <sup>¶</sup>	Standard Deviation	Coefficient of Variation
		_____	µg / g _____	%
P	Olsen	10.2	0.99	9.71
	Ke	15.3	1.06	6.93
	KM	10.5	0.75	7.14
	BM	18.4	1.36	7.39
K	Olsen	119.0	10.97	9.22
	Ke	97.3	3.78	3.88
	KM	109.8	7.78	7.09
	BM	120.5	6.31	5.24

<sup>¶</sup> Represents 12 daily extractions of P and 11 daily extractions of K for each extractant.

Phosphorus and potassium extracted by the three selected methods and by the Olsen method were all highly and significantly correlated. The correlation coefficients (r) of Olsen P with Ke-P, KM-P and BM-P were 0.91, 0.92 and 0.87, respectively (Table 3).

The correlation coefficients of Olsen K with Ke-K, KM-K and BM-K were 0.95, 0.85 and 0.87, respectively (Table 4).

Table 3. Correlations of three extractants with Olsen for available P (n = 253).

Extractant	Range of value µg/g	Regression equation	Correlation coefficient
Olsen	3.3 - 50.0		
Ke	3.3 - 83.7	$Y^{\P} = -1.38 + 1.41x^{\S}$	0.91**
KM	1.5 - 47.2	$Y = 0.82 + 0.91x$	0.92**
BM	0.8 - 125.0	$Y = -4.17 + 2.02x$	0.87**

$\P$  P extracted by indicated extractant.

$\S$  P extracted by Olsen.

\*\* Significant at P<0.01 level.

Table 4. Correlations of three extractants with Olsen for exchangeable K (n = 353)

Extractant	Range of value µg/g	Regression equation	Correlation coefficient
Olsen	43 - 827		
Ke	63 - 730	$Y^{\P} = 12.34 + 0.95x^{\S}$	0.95**
KM	53 - 993	$Y = -31.61 + 1.55x$	0.85**
BM	75 - 921	$Y = -28.47 + 1.63x$	0.87**

$\P$  K extracted by indicated extractant.

$\S$  K extracted by Olsen.

\*\* Significant at P<0.01 level.

The amount of P and K extracted by the four methods used in the study were different (Tables 3 and 4). KM extracted similar amount of P as did Olsen but about 1.5 times more K than Olsen. Ke removed about 1.4 times more P than 0.5N NaHCO<sub>3</sub> but similar amount of K as 0.5N NaHCO<sub>3</sub>. BM-extractable P and K were about 2X and 1.6X more than Olsen-extractable P and K, respectively. Our result of a 1.4X more P removed from Ke than Olsen (Table 3) showed some inconsistency with the previous study (van Lierop, 1988) in which a 2.5 times more P was extracted by Ke than Olsen. The reason of this difference is unclear, maybe due to the different types of soils used. In the van Lierop (1988) study, 51% of 78 soils used had pH values from 4.2 to 6.9. The pH of the 400 soils used in our study ranged from 5.5 - 8.4. Among these soils, only 15.7% had pH values between 5.5 and 6.5. The majority of soils (76%) had pH values larger than 7.0 in which 72.7% had pH values from 7.5 to 8.4. Bicarbonate solution was relatively easier to extract proportional amount of P from neutral and alkaline soils than from acid soils (Shi, 1980 and van Lierop 1988).

It was interesting that KM which originated from Ke only extracted 2 / 3 as much P as Ke itself (Fig. 1). The change of the proportion of P seemed to be caused by the addition of 0.25N NH<sub>4</sub>OAc. It may have resulted from the increase of pH from 3.2 to 4.9

due to this neutral salt solution added. Mehlich (1988a) reported that extractable P increased with increasing concentration of acid in Ca-P predominant soil, but the acid used in Mehlich's study was HCl.

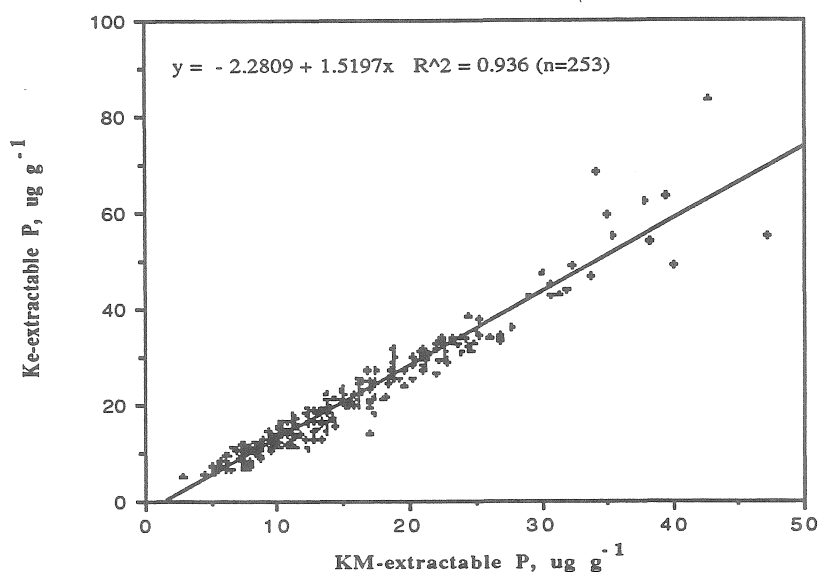


Figure 1. Relationship between KM and Ke extracted P levels.

Results from K extraction confirmed our expectation that K release increased with the introduction of  $\text{NH}_4^+$  (Table 4 and Fig. 2). The levels of K extracted by KM were two-fold those extracted by Ke. Furthermore, KM removed nearly 1.4X more K than Ke in the soils with less than  $300 \mu\text{g g}^{-1}$  of K extracted by Olsen.

### Influence of Soil pH on P and K Extracted by Different Solutions

Phosphorus and K extracted by Olsen and by each of the methods tested were highly and significantly correlated when all soils studied were included in the correlations (Table 3 and 4). In order to ascertain the effect of pH on the relationship between levels extracted by various extractants, the soils were separated into three groups on the basis of their pH, i.e., acid soils (pH from 5.5 to 6.2), neutral and near neutral soils (pH from 6.7 to 7.3) and alkaline soils (pH from 7.8 to 8.4).

The phosphorus levels extracted by the three extractants tested were highly significantly correlated with those extracted by the Olsen extractant, especially at pH levels from 6.7 to 7.3 and from 7.8 to 8.4 (Table 5). In alkaline soils, levels of P extracted by Ke and BM were generally better correlated with those extracted by Olsen than levels extracted by BM did. Since the Olsen method extracts somewhat greater amounts of P from neutral and alkaline soils than from acid soils (Shi, 1980 and van Lierop 1988), it may indicate that the efficiency of P extraction by all three methods tested was similar and was not much affected by different pH levels.

The levels of K extracted by all three extractants tested were highly significantly correlated with those extracted by the Olsen extractant in acid and neutral soils, but levels extracted by KM and BM did not correlate as well as Ke in alkaline soils (Table 6). Table 6 also showed that extracted levels of K increased with the increase of soil pH by the KM

and BM extractants. The levels of K extracted by KM and BM from alkaline soils were nearly 1.3X those extracted from acid soils.

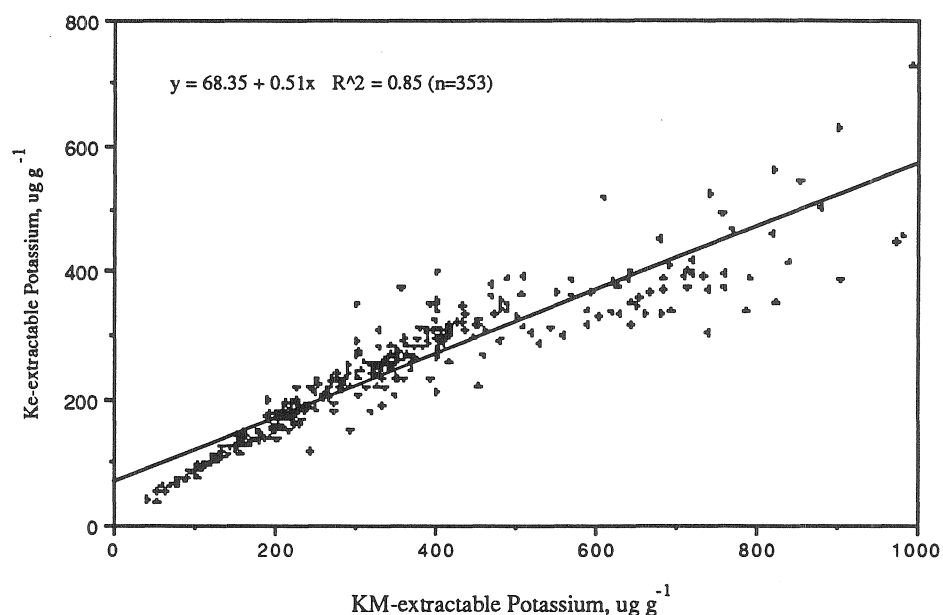


Figure 2. Relationship between KM and Ke extracted K levels.

Table 5. Comparison of the slope and  $R^2$  of the regression between the P levels extracted by the three methods tested and those extracted by the Olsen method at different soil pH levels.

Soil pH range	No. of samples	Phosphorus extracted by						
		Olsen μg/g	Ke		KM		BM	
			Slope	R <sup>2</sup>	Slope	R <sup>2</sup>	Slope	R <sup>2</sup>
5.5 - 6.3	37	6.7 - 34.2	1.49	0.81**	0.98	0.79**	2.05	0.84**
6.7 - 7.3	63	4.6 - 31.2	1.47	0.90**	1.03	0.90**	1.86	0.86**
7.8 - 8.4	141	3.3 - 40.2	1.28	0.85**	0.95	0.84**	1.56	0.76**

\*\* Significant at  $P < 0.01$  level.

Table 6. Comparison of the slope and  $R^2$  of the regression between the K levels extracted by the three methods tested and those extracted by the Olsen method at different soil pH levels.

Soil pH range	No. of samples	Olsen $\mu\text{g/g}$	Potassium extracted by					
			Ke		KM		BM	
			Slope	$R^2$	Slope	$R^2$	Slope	$R^2$
5.5 - 6.3	37	43 - 617	0.88	0.98**	1.30	0.97**	1.24	0.97**
6.7 - 7.3	67	56 - 536	0.98	0.97**	1.50	0.94**	1.47	0.97**
7.8 - 8.4	149	52 - 827	0.99	0.85**	1.70	0.68**	1.67	0.69**

\*\* Significant at  $P < 0.01$  level.

### Influence of Soil Texture on P and K Extracted by Different Methods

In Saskatchewan soils, soil texture varies widely, hence, the suitability of a new method to replace the Olsen, assuming that the latter is the appropriate one, must be judged on how well it performs in relation to the Olsen extractant in all types of texture. To test the influence of soil texture on extractable P and K by the three methods tested, correlations were drawn with Olsen-extractable levels for the sand, loam and clay soil types only.

The correlations between the levels of P extracted by the three methods tested and those extracted by the Olsen method were highly significant for all types of texture (Table 7). It has been shown that the Olsen extractant removes P consistently within a wide range of texture (Holford, 1980 and Thomas et al., 1973). The data from Table 7 also show that more P was extracted in sandy soils than in clay soils by all three solutions tested. Therefore, soil texture influences the amount of P extracted by all three methods tested.

Table 7. Comparison of the slope and  $R^2$  of the regression between the P levels extracted by the three methods tested and those extracted by the Olsen method for different textural groups.

Texture	No. of samples	Olsen $\mu\text{g/g}$	Phosphorus extracted by					
			Ke		KM		BM	
			Slope	$R^2$	Slope	$R^2$	Slope	$R^2$
Sand	69	4.6 - 40.0	1.88	0.86**	1.16	0.93**	2.76	0.79**
Loam	137	4.7 - 40.3	1.37	0.90**	0.94	0.88**	1.77	0.81**
Clay	73	4.7 - 34.2	1.28	0.84**	0.84	0.82**	1.53	0.91**

\*\* Significant at  $P < 0.01$  level.

The correlations between K levels extracted by the three methods tested and those extracted by Olsen method were highly significant for all three textural groups. However, the highest correlation was consistently obtained between Ke and Olsen extractable K levels (Table 8).

Table 8. Comparison of the slope and  $R^2$  of the regression between the K levels extracted by the three methods tested and those extracted by the Olsen method for different textural groups.

Texture	No. of samples	Olsen $\mu\text{g/g}$	Potassium extracted by					
			Ke		KM		BM	
			Slope	$R^2$	Slope	$R^2$	Slope	$R^2$
Sand	81	43 - 388	0.83	0.91**	1.10	0.78**	1.16	0.81**
Loam	161	78 - 616	0.96	0.83**	1.35	0.88**	1.32	0.87**
Clay	61	64 - 827	0.78	0.85**	1.18	0.43**	1.15	0.55**

\*\* Significant at  $P < 0.01$  level.

#### Influence of Soil Zones on P and K Extracted by Different Methods

Levels of P extracted by three methods tested were all highly and significantly correlated with those extracted by the Olsen method when the soils used were separated on per soil Zone basis (Table 9). The results from the K extraction, however, were quite different. The correlations between the levels extracted by all three methods tested with those extracted by the Olsen method were quite lower for the Brown and Grey soils for the soils of the other four soil Zones. Of the three methods tested, levels extracted by the Ke method were better correlated with those extracted by the Olsen method (Table 10).

Table 9. Comparison of the slope and  $R^2$  of the regression between the P levels extracted by the three methods tested and those extracted by the Olsen method for different soil Zones.

Soil Zone	No. of samples	Olsen $\mu\text{g/g}$	Phosphorus extracted by					
			Ke		KM		BM	
			Slope	$R^2$	Slope	$R^2$	Slope	$R^2$
Dark Brown	107	4.6 - 42.0	1.34	0.83**	0.94	0.81**	1.81	0.82**
Brown	60	4.7 - 50.0	1.20	0.89**	0.82	0.89**	1.55	0.92**
Gray	16	7.0 - 26.3	2.41	0.84**	1.49	0.85**	3.48	0.82**
Gray Black	51	5.9 - 40.3	1.30	0.87**	0.99	0.92**	1.63	0.74**
Thin Black	73	6.3 - 44.5	1.39	0.91**	0.91	0.90**	1.78	0.85**
Thick Black	19	4.5 - 31.2	1.47	0.95**	0.99	0.91**	1.95	0.96**

\*\* Significant at  $P < 0.01$  level.



Table 10. Comparison of the slope and  $R^2$  of the regression between the K levels extracted by the three methods tested and those extracted by the Olsen method for different textural groups.

Soil Zone	No. of samples	Olsen $\mu\text{g/g}$	Potassium extracted by					
			Ke		KM		BM	
			Slope	$R^2$	Slope	$R^2$	Slope	$R^2$
Dark Brown	116	87 - 827	0.97	0.84**	1.55	0.67**	1.47	0.71**
Brown	45	113 - 402	0.63	0.57**	1.10	0.20**	1.57	0.42**
Gray	18	51 - 550	0.36	0.68**	0.61	0.73**	0.65	0.72**
Gray Black	60	43 - 347	0.86	0.95**	1.26	0.86**	1.29	0.90**
Thin Black	89	70 - 585	0.82	0.86**	1.27	0.84**	1.25	0.87**
Thick Black	24	80 - 380	0.71	0.94**	1.33	0.87**	1.15	0.93**

\*\* Significant at  $P < 0.01$  level

## CONCLUSIONS

Results from this study showed that either P or K levels extracted by the three methods tested were highly and significantly correlated to those extracted by the Olsen method. The relationships between P levels extracted by the three methods tested and those extracted by the Olsen method were not affected by soil pH, soil texture and soil Zone. The relationships among K levels extracted by the three methods tested and those extracted by the Olsen method, however, were influenced to a varying degree by different soil conditions.

As expected, the addition of 0.25N  $\text{NH}_4\text{OAc}$  to Ke extractant increased the concentration of extracted K, but the relationship of levels extracted by KM with those extracted by Olsen was not as good as that between Ke-extracted levels and those extracted by the Olsen method. Ke seemed to be the most appropriate procedure for simultaneous extraction of P and K when considering only its correlation with the Olsen method. Which of the three studied method could serve as a replacement for the Olsen in the future? The answer will rely on a further study to calibrate the different soil extractant levels with plant response in the greenhouse or in the field.

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