

AN EVALUATION OF TWO CHEMICAL METHODS FOR
THE DETERMINATION OF POTASSIUM IN SOILS

by 632

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INTRODUCTION

Potassium has been recognized as being important in crop production since the early 1800's, but extensive investigations by soil chemists to characterize the forms and behavior of soil potassium, to discover its relationship to plant growth, and to predict the potassium fertilizer requirements of soils by chemical analyses began only about four decades ago.

Soil chemists first attempted to predict which soils required potassium fertilizer on the basis of a total soil analysis for potassium. These methods proved inadequate, however, since the bulk of soil potassium is contained in primary minerals and in clay lattice structures. These forms of potassium are not usable by plants, except for very small quantities, and correlation between predicted crop response and actual crop response to potassium fertilizer was low.

After extensive experimentation with various extracting solutions and techniques, some designed to closely simulate the potassium extracting ability of a plant, most soil workers agreed the "exchangeable" form of soil potassium was most indicative of a soils need for fertilizer.

Ultimately, relatively accurate and dependable techniques for measurement of exchangeable potassium were developed, but these techniques were slow, complicated, and tedious.

The acceptance by farmers of the soil test as a valuable diagnostic tool in crop production made necessary a rapid, simple, and inexpensive test procedure to be used in practical, routine soil testing laboratories.

Advances in instrumentation, notably the flame spectrophotometer, greatly improved soil testing procedures for potassium in the realm of

speed, simplicity, and accuracy. Laboratories with sufficient financial support adopted these methods. The simplified, or rapid, flame emission spectrophotometer method has been used in the Kansas State University state soil testing laboratory since 1949. Cost of instrumentation prohibits the use of this method in laboratories operated by Kansas county agricultural agents. In these laboratories the inexpensive turbidimetric solid cobalt-nitrite method as modified by Olson (16) has been in use since 1949.

As cultivation of the soil and potassium removal by crops continues, the quantity of easily weathered potassium-bearing minerals gradually declines. With crop yields continually rising and with increasing dependence upon highly resistant minerals, the level of available potassium is becoming increasingly important and more critical. Doubt existed as to whether the two above-mentioned methods of testing soils for potassium were in acceptable agreement to meet present requirements.

The study reported in this thesis was undertaken to evaluate the two methods currently used in Kansas for determining exchangeable soil potassium, to gain insight into the reason for possible discrepancies between the results of the two tests, and to add to the general knowledge of this subject.

REVIEW OF LITERATURE

The term exchangeable potassium, as it is generally considered in a qualitative sense, is that potassium which is adsorbed, and readily available to plants, on mineral and organic soil components and which is in equilibrium with fixed potassium and water soluble potassium.

FIXED K $\frac{1}{--7}$ EXCHANGEABLE K $\frac{1}{--7}$ WATER SOLUBLE K

Exchangeable potassium is more difficult to define quantitatively, however, primarily because there is no sharp demarcation between fixed and exchangeable potassium (3). The quantity found, therefore, depends to a degree upon the method of measurement, the exchanging ion, and the soil involved. However, by convention it is generally agreed that exchangeable potassium is that amount of potassium which may be extracted from a soil by normal ammonium acetate at pH 7, minus that which is water soluble.

Merwin and Peech (14) advocated normal ammonium acetate as the standard for extraction of exchangeable potassium because ammonium causes closure of the spaces between the highly charged clay layers and prevents the release of nonexchangeable potassium to the exchangeable form during extraction. Ammonium acetate also has other practical advantages to recommend it (11).

Prior to and since the adoption of this convention, however, a large number of techniques have been developed in an effort to more closely predict the potassium fertilizer requirement of a soil (2). Liebig's concept that total soil potassium was indicative of a soils fertilizer requirement was abandoned when advances in colloidal chemistry and clay mineralogy proved the complexity of soil potassium relations and of

potassium release over time to growing plants (4). Even while Liebig's concept was in vogue, early soil chemists experimented with extracting solutions in an effort to determine immediately available potassium supplies (15).

From 1845 to the present, a large number of different potassium extracting solutions and techniques have been employed. These include: acids varying in strength; distilled water; carbonated water; chloride salts, nitrates, and acetates of the alkali and alkaline-earth metals and of ammonium; sodium tetraphenylboron; electrolysis; procurement of the soil solution by displacement with another liquid; procurement of a soil extract by dialysis through collodion sacks; resin exchange columns. There has been considerable variation in testing procedures and various combinations of extracting solutions have been employed.

Presently, the chemistry of potassium fixation is relatively well understood but the related phenomenon of potassium exchange, even after extensive investigation, remains only partially explained. Literature on the various facets of potassium exchange is voluminous but summary works and review articles are available e.g. Reitemeir (18) and Wiklander (23).

The exchange of potassium for another cation at adsorption sites on soil particles is related to, among other things, the degree of hydration of the ions involved. The replacing power of a cation has often been found to increase in the same order as the lyotropic series, viz. $\text{Li} < \text{K} = \text{NH}_4 < \text{Rb} < \text{Cs} < \text{H}$ and for the alkaline-earth ions, $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$. The position of the monovalent and divalent ions in a combined series, however, has proved to vary considerably with the nature of the exchanger and the concentration of the solution (24), but the relative replacing power

often follows the order $M^+ < M^{++} < M^{+++} < M^{++++}$ since the adsorption energy of a cation increases with increased valence.

However, after much experimentation it has become evident that there is no single universal order of the replacing power of cations and that the hydration concept alone is unsatisfactory (8). Rather, the replacing power of a cation is determined to a greater or lesser degree by the following: the nature and amount of soil mineral and organic matter; the degree of exchange capacity neutralization in relation to the exchanging solution concentration; the valence, hydrated and nonhydrated size, polarizability and polarizing power of the ions involved; the concentration of the replacing ion; the nature and amount of complementary adsorbed ions. Rich (19) found the pH of the system to also be a factor.

Thus, the relative replacing power or rank ascribed to a given cation by one investigator may not, and in actuality, generally has not agreed with the rank given the same cation by another investigator under different experimental conditions.

Studies comparing the effectiveness of ammonium and sodium in exchanging potassium from soil have shown ammonium generally is most efficient in single equilibrium extractions but that sodium may be most efficient when liberated potassium is removed from the system as by leaching or successive extractions.

A number of investigators have studied potassium removal by ammonium and sodium utilizing single equilibrium extractions. Ogot (P.O. Ogot, 1966. Chemical measurements of potassium availability in soil. M.S. Thesis. University of Vermont) found that sodium acetate was as much as 50% less effective than ammonium acetate in removing exchangeable potassium from medium to fine textured soils of Vermont and Missouri but that the two

extractants gave comparable results on some lighter soils. Ammonium acetate gave a better measure of available potassium in clay soils as indicated by plant uptake.

McIntosh (13), using ten Vermont soils having different parent materials and representing the major soil types in Vermont showed ammonium removed more potassium than did sodium in every instance and that the relationship between the two extractants did not remain constant. Although sodium satisfactorily removed potassium from sandy soils, the investigator considered it unsatisfactory for routine testing in areas where soils are variable due to its inability to remove a proportionate amount of potassium from clay soils. Therefore, it was proposed that ammonium extraction would provide a more useful measure of available potassium.

In a comparison of the ammonium acetate - flame spectrophotometric method versus the sodium nitrate - sodium cobaltinitrite turbidimetric method, Bohannon (4), using Illinois soils, found the two methods did not yield the same absolute values for exchangeable potassium. In general, sodium nitrate was less efficient than ammonium acetate in the extraction of exchangeable potassium from moist soils but as soil moisture decreased (soils were dried under controlled relative humidity conditions) the efficiency of sodium nitrate increased and was, in some instances, greater than that of ammonium acetate. Agreement between the two methods was especially poor on soils low in exchangeable potassium. This was attributed to the low sensitivity of the sodium cobaltinitrite method at low potassium concentrations.

According to Garmen (7), the amounts of exchangeable potassium removed from surface soils and from subsoils by continuous cropping was highly correlated with amounts removed by both sodium acetate and ammonium acetate, but potassium removal by sodium was approximately 80% that removed

by ammonium from surface soils and less than 80% for subsoils.

Several investigators have studied potassium removal by ammonium and sodium utilizing leaching or successive extraction techniques. Merwin and Peech (14) leached four widely different New York soils with successive portions of sodium acetate and ammonium acetate. The amount of potassium exchanged was greater for sodium than for ammonium. The first leachate (200 ml) of ammonium acetate contained over 90% of the total potassium removed in the combined leachates (1000 ml). This clear cut separation of exchangeable potassium was attributed to the blocking effect of ammonium ions (i.e. closure of the mineral lattice upon ammonium penetration) and was in sharp contrast to the continued extraction of potassium by sodium acetate.

Using successive extractions, Williams and Jenny (25) found the effectiveness of sodium to be greater than ammonium in replacing potassium from Ramona loam. Sodium continued to replace potassium following the first three extractions but ammonium did not. It was noted that the potassium which was available for exchange with ammonium evidently was a fixed quantity occupying external or easily available positions on the surfaces of the mineral particles.

Whether subjected to successive or to single extractions, illite exchanged more potassium for ammonium than for sodium according to Bolt, Sumner, and Kamphorst (5). Upon successive extraction, illite continued to release relatively significant amounts of potassium to sodium but not to ammonium. However, the results were reversed, i.e. ammonium continued to extract potassium while sodium did not, when a single but prolonged extraction was employed. These findings prompted the investigators to suggest an explanation for the disparity between amounts of potassium

removed by single equilibrium extractions and amounts removed by leaching or repeated extractions. It was proposed that the potassium ions present in the clay studied should be divided into three categories, viz.,

1. Potassium ions which occupy surface exchange sites, i.e., the outer planer surfaces of the clay mineral; these ions can be rapidly replaced by all cations (within 1 hour) and the sites involved here are not very specific for potassium ions.
2. Potassium ions which occupy interlattice positions near the edges of the clay particles; these sites are very specific for potassium and ammonium ions (and possibly certain other cations); exchange against ammonium is rapid. Replacement by other ions is very difficult because of a very unfavorable equilibrium constant so that renewal of the extractant to remove liberated potassium is necessary for replacement to proceed.
3. Potassium ions which occupy interlattice positions away from the edge of the particles; these sites are again very specific for ammonium and potassium but the exchange is now determined by a moderately slow film diffusion process.

To the third category of potassium was attributed not only the increase in the amount of potassium exchanged against ammonium ions in the second and subsequent extractions, but also part of the potassium released by prolonged shaking with ammonium. Lack of potassium exchange with sodium during prolonged shaking was attributed to the competition between liberated potassium (category II) and sodium for exchange sites, i.e. the unfavorable equilibrium constant; the increase in amount exchanged in second and subsequent extractions was considered to be the result of shifting the potassium equilibrium by removal of liberated potassium.

Rich and Black (20) investigated the nature and location of the specific sorption sites which Bolt et al. (5) had categorized (Category II). It was proposed that exchangeable potassium is frequently located in wedge-shaped spaces in the interlayers of weathered micas. Extent of potassium exchange depends largely on the diameter of the exchanging solvated cation and the pH of the system. Hydrated cations larger than potassium, such as sodium, are too large to enter the interlayer space but cations the size of potassium, such as ammonium, can enter and effectively replace potassium.

Various studies (4) (6) (9) (12) and (22) have shown that, generally, exchangeable potassium levels increase as a moist soil is dried, and that as air-dry moisture levels are reached, the increase is usually disproportionately greater and often abrupt. Conversely, it has been shown that, generally, if dried soils are rewet to field capacity or above, potassium fixation will occur, i.e. reversion (1) (10) (12) and (21). However, few have studied the extent of both potassium release and reversion occurring within or near the moisture content range of air-dried soils.

Luebs, Stanford, and Scott (12) reported that exchangeable potassium levels can fluctuate rather drastically in response to relatively minor changes in soil moisture percent when the moisture is near that of an air-dried soil. These investigators found that the exchangeable potassium levels of three air dry soils used as analytical controls in the Iowa soil testing laboratory, and subjected to its variable temperature and humidity, tended to be inversely proportional to the changes in water vapor pressure within the laboratory. From March to August the exchangeable potassium content of the Marshall soil decreased from 380 pounds to approximately 260 pounds per acre; Webster soil decreased from approximately 260 pounds

per acre to 110 pounds per acre; Edina showed the least decrease during this period (approx. 40 pounds per acre). In addition, it was shown that by placing Edina soil in desiccators under high or low vapor pressure, a corresponding change in the level of exchangeable potassium would result. Interchanging the samples resulted in readjustment of potassium levels to near those previously attained, with most of the adjustment occurring within 20 days.

EXPERIMENTAL EQUIPMENT

Primary instruments used in this study included: (1) Perkin-Elmer flame emission spectrophotometer for the direct determination of potassium in soil extract solutions; (2) Coleman Junior Model 6A absorption spectrophotometer for the turbidimetric determination of potassium cobaltinitrite precipitate.

EXPERIMENTAL PROCEDURE

Collection and Preparation of Soil Samples

The soil samples were obtained through the cooperation of county agents in selected counties over the state of Kansas. The sampling procedure was as follows:

1. Each county agent was asked to send five samples.
2. Some of the samples were to be from areas considered to be low in fertility.
3. Samples were to be taken from the surface soil in the same manner as for general fertility tests.
4. The size of the sample was to be one quart.

The soil samples were air dried at room temperature, ground to pass through a 40 mesh sieve, and thoroughly mixed.

Exchangeable Potassium Determination by the Turbidimetric Solid Cobaltinitrite Method (County Method)

The procedure used was as follows:

1. Ten grams of soil were weighed into a 125 ml. erlenmeyer flask.
2. Twenty milliliters of 25% sodium nitrate extracting solution were added and the mixture shaken vigorously for one minute.

3. The mixture was filtered through a fluted filter paper and five milliliters of the filtrate were pipetted into a funnel tube.
4. A blank sample was prepared by placing five milliliters of extracting solution into a funnel tube.
5. Three milliliters of isopropyl alcohol were added to the filtrate and blank extracting solution, the funnel tubes stoppered, and contents mixed by shaking.
6. One-tenth gram sodium cobaltinitrite was placed in the funnel tubes, the tubes stoppered, contents mixed by vigorous shaking, and the time noted.
7. After approximately three to five minutes had elapsed, the tube containing the blank was placed in the absorption spectrophotometer and the instrument adjusted to read zero optical density (100% T) using a wave-length of 700 mu.
8. The tube containing the soil extract was placed in the instrument, the optical density reading recorded, and by reference to a standardization curve previously determined using solutions containing known quantities of potassium, the pounds per acre of exchangeable potassium was determined.

Exchangeable Potassium Determination by the Rapid
Flame Emission Spectrophotometer Method (State Method)

The procedure used was as follows:

1. Five grams of soil were weighed into a 125 ml. erlenmeyer flask.
2. Twenty-five milliliters of 1 N ammonium acetate extracting solution were added, the mixture was shaken vigorously for ten minutes on a mechanical wrist-action shaker and then filtered through a fluted filter paper.

3. After adjustment of the photometer with standard potassium chloride solutions in ammonium acetate, the soil filtrate was passed through the instrument and the reading recorded. By reference to the standardization curve, the pounds of exchangeable potassium per acre was determined.

RESULTS AND DISCUSSION

Soil Exchangeable Potassium Levels: Rapid Flame Emission Spectrophotometer Method vs. Turbidimetric Solid Cobaltinitrite Method

The rapid flame emission spectrophotometer method and the turbidimetric sodium cobaltinitrite method as modified by Olson (16), (hereafter referred to as the flame photometric method and the turbidimetric method) were used to analyze for exchangeable potassium in 97 soils from selected counties in Kansas. Results are shown in Table 1. The soils were analyzed by the flame photometric method in June and July 1965, and by the turbidimetric method in August 1965. Average results of all soils were 533 and 412 pounds of exchangeable potassium per acre, respectively. Soils were divided into three categories depending upon their exchangeable potassium content: Category I - less than 161 pounds/acre; Category II - equal to or greater than 161 pounds/acre but less than or equal to 320 pounds/acre; Category III - greater than 320 pounds/acre. Since a given soil was rejected if both of its exchangeable potassium values being compared did not fall into the same category, the total number of soils analyzed, as reported in the appendix, was greater than that noted in the discussion. Statistical analyses showed results obtained by the flame photometric method and the turbidimetric method are significantly different in each of the three categories at the .01 level of probability. Results of further analyses reported on succeeding pages tend to confirm that the wide differences in results between the two methods in this comparison test were not due to inherent differences in the two soil testing techniques but, rather, to the effects of storage on the soil samples.

In April 1966, thirty soils were selected for an additional comparison

test between the flame photometric and the turbidimetric methods (Table 2). Average results for all soils were 300 and 282 pounds of exchangeable potassium per acre, respectively. Good agreement exists with soils in Categories I and II; agreement was somewhat poorer with soils in Category III but was within the limits of acceptability for many practical purposes. Statistical analyses show results of the flame photometric and the turbidimetric methods did not differ significantly in regard to soils in Category I and II but Category III results differed significantly at the .01 level of probability.

Table 1. Exchangeable potassium as determined by the flame photometric method in June-July 1965 and the turbidimetric method in August 1965 in 97 soils from selected counties in Kansas.

| Soil Category [†] | Flame Photometric Method, June-July/'65 pounds/acre | Turbidimetric Method, Aug./'65 pounds/acre |
|--|---|--|
| Category I | 139** | 97** |
| Category II | 270** | 200** |
| Category III | 702** | 547** |
| Avg. of all soils (Cat. I, II, and III) | 533** | 412** |

** Differences between methods are significant at the 0.01 level of probability.

† Soils divided into three categories depending upon their exchangeable potassium content: Category I - less than 161 pounds/acre; Category II - equal to or greater than 161 pounds/acre but less than or equal to 320 pounds/acre; Category III - greater than 320 pounds/acre.

Table 2. Exchangeable potassium as determined by the flame photometric method in April 1966 and the turbidimetric method in April 1966 in 30 soils from selected counties in Kansas.

| Soil Category [†] | Flame Photometric Method, April/'66 pounds/acre | Turbidimetric Method, April/'66 pounds/acre |
|--|---|---|
| Category I | 126 | 127 |
| Category II | 223 | 225 |
| Category III | 504 ^{**} | 453 ^{**} |
| Avg. of all soils (Cat. I, II, and III) | 300 [*] | 282 [*] |

* Exchangeable potassium values derived from averaging all determinations by each method are significantly different at the 0.05 level of probability.

** Exchangeable potassium values derived from averaging all determinations by each method on soils in Category III are significantly different at the 0.01 level of probability.

† Soils divided into three categories depending upon their exchangeable potassium content. Refer to Table 1 footnote.

Influence of Soil Storage on Exchangeable Potassium Level

The flame photometric method was used to analyze 36 soils for exchangeable potassium in June-July 1965, and again in April 1966 (Table 3). Exchangeable potassium decreased significantly, from 407 to 332 pounds/acre, during the period and differences were significant in all three soil categories.

The turbidimetric method was used to analyze 103 soils for exchangeable potassium in August 1965, and again in September 1965 (Table 4). Mean values obtained were 387 pounds/acre vs. 359 pounds/acre for the earlier and later date, respectively. Soils relatively high in potassium i.e. soils in Category III, and to a lesser degree, Category II, were responsible

for this significant difference; Category I soils did not exhibit a statistically significant difference.

Forty-five of the 103 soils were analyzed again turbidimetrically in April 1966. Average results for the August 1965, September 1965, and April 1966 testing dates were, respectively, 275, 265, and 296 pounds/acre exchangeable potassium. A separate three-date vs. exchangeable potassium level analysis of only these soils was performed. In contrast to the above, the average exchangeable potassium content of this group of soils did not change significantly between August and September 1965. However, a significant increase over both of these dates was shown in April 1966. That no significant difference was shown between August and September 1965 in the combined analysis of this sub-group of soils might be expected since 20% of these soils were of the Category I class which were nearly identical in exchangeable potassium content in August as compared to September 1965.

It is believed insidious changes in the moisture content of the soils were responsible for the change in exchangeable potassium levels with time. This is in agreement with results reported by Leubs et.al. (12) and Bohannon (4). Each bulk soil sample was stored in cylindrical pint ice cream containers. Such containers are not impervious to moisture. Furthermore, the samples were serving two separate research studies; samples were directly exposed to the atmosphere at relatively frequent intervals when the containers were opened and the sample stirred simultaneous to removal of subsamples for the separate analyses.

Table 3. Influence of storage on the exchangeable potassium level of 36 soils from selected counties in Kansas as measured by the flame photometric method in June-July 1965 and April 1966.

| Soil Category [†] | Flame Photometric Method | |
|--|--------------------------|-------------|
| | June-July/'65 | April/'66 |
| | pounds/acre | pounds/acre |
| Category I | 142** | 113** |
| Category II | 248** | 209** |
| Category III | 633** | 511** |
| Avg. of all soils (Cat. I, II, and III) | 407** | 332** |

** Differences between methods are significant at the 0.01 level of probability.

† Soils divided into three categories depending upon their exchangeable potassium content. Refer to Table 1 footnote.

Table 4. Influence of storage on the exchangeable potassium level of 103 soils from selected counties in Kansas as measured by the turbidimetric method in August 1965 and September 1965.

| Soil Category [†] | Turbidimetric Method | |
|--|----------------------|-------------|
| | Aug./'65 | Sept./'65 |
| | pounds/acre | pounds/acre |
| Category I | 125 | 125 |
| Category II | 231** | 223** |
| Category III | 574** | 525** |
| Avg. of all soils (Cat. I, II, and III) | 387** | 369** |

** Differences between methods are significant at the 0.01 level of probability.

† Soils divided into three categories depending upon their exchangeable potassium content. Refer to Table 1 footnote.

Coefficients of Variation for the Flame Photometric Method vs. Turbidimetric Method

All exchangeable potassium values reported in this thesis are averages of at least two determinations. It was apparent that successive exchangeable potassium determinations on any given soil by the flame photometric method were in closer agreement to each other than those obtained using the turbidimetric method. To contrast this dispersion in the values obtained by the two different procedures, coefficients of variation were computed using the first two exchangeable potassium values obtained by each procedure.

The average coefficient of variation (Table 5) derived from 222 determinations for each testing procedure on the same 111 soils was as follows: June-July 1965, flame photometric method, 1.838%; August 1965, turbidimetric method, 3.574%; September 1965, turbidimetric method, 4.064%. The average coefficient of variation derived from 70 determinations for each method on the same 35 soils was as follows: April 1966, flame photometric method, 3.273%; April 1966, turbidimetric method, 5.933%. The coefficient of variation for the turbidimetric and flame photometric methods (weighted mean) are 4.107% and 2.182%, respectively. Therefore, within the context of the above, the turbidimetric method of determining soil exchangeable potassium levels is only approximately one-half as precise as the flame photometric method i.e. a single exchangeable potassium determination value has approximately twice as great a chance of corresponding to the mean of multiple determination values when the flame photometric method is used as when the turbidimetric method is used.

A source of difficulty with the turbidimetric method was the relative non-reproducibility of the standardization curve. Other workers (16) (17)

have reported the optical density reading to be dependent upon the particle size and solubility of the precipitate, as well as the color of the solution phase. Since these in turn are dependent upon the conditions of analysis, apparently these and other variations e.g. presence of interfering ions, were acting to cause a greater dispersion in the measured soil exchangeable potassium values and thus, as reported above, a greater coefficient of variation.

Table 5. Coefficients of variation (percent) for the turbidimetric and flame photometric method.

| Testing Date | Flame Photometric Method | Turbidimetric Method |
|-------------------------------|--------------------------|----------------------|
| June-July/'65 | 1.838 | --- |
| August/'65 | --- | 3.574 |
| September/'65 | --- | 4.064 |
| April/'66 | 3.273 | 5.933 |
| Weighted Average [†] | 2.182 | 4.107 |

[†] Identical group of 111 soils tested by both methods in 1965; identical group of 35 soils tested by both methods in 1966.

Effect of Variation in Weight of Sodium Cobaltinitrite Powder used in the Turbidimetric Method

Gross errors (100%) in sodium cobaltinitrite powder measurement will result in only slight changes in optical density readings so long as both the blank solution used to zero the photometer, and the sample containing the potassium, receive the same amount of powder (16).

However, using the following procedure,

1. Ninety milligrams (.090g) of cobaltinitrite powder was added to one of 11 tubes containing 45ppm potassium standard solution.

2. Cobaltinitrite powder was added to the other 10 tubes in amounts ranging upwards from .092g to .110g, inclusive, in increments of .002g.
3. Optical density reading of spectrophotometer was adjusted to .50 with the sample containing .090g powder in the instrument.
4. Optical density of the 10 remaining samples was then determined.

It was found (Table 6) that for any given percentage error in measuring the sodium cobaltinitrite powder, e.g. 10% error, an average percentage error of approximately two-thirds this amount ($6\frac{2}{3}\%$) would occur in determined exchangeable potassium values. Consequently, all turbidimetric determinations reported in this thesis were with weighed portions (.1g) of sodium cobaltinitrite powder rather than with portions determined with a volumetric measure.

Data in Table 6 would indicate that a slightly greater variation in exchangeable potassium values (O.D. readings) would result, with a concomitant increase in coefficients of variation, if the less accurate volumetric method (rather than the weighing method) of powder measurement were used, as is the practice in county soil testing laboratories.

Table 6. Effect of variations in amount of solid sodium cobaltinitrite on optical density readings and determined pounds per acre of exchangeable potassium after setting photometer to .50 optical density with the .090g sample.

| | | | | | | | | | | | |
|--------------------------------------|------|------|------|------|------|------|------|------|------|------|------|
| Sodium cobalti- nitrite, grams | .090 | .092 | .094 | .096 | .098 | .100 | .102 | .104 | .106 | .108 | .110 |
| 45ppm K solution, optical density | .500 | .505 | .510 | .510 | .515 | .520 | .520 | .530 | .538 | .550 | .545 |
| Exchangeable K, pounds per acre | 145 | 149 | 151 | 151 | 154 | 156 | 156 | 160 | 163 | 168 | 166 |

CONCLUSIONS

Results of the experimental work reported in this thesis may be summarized as follows:

1. Exchangeable potassium determinations by the flame photometric (state) method and the turbidimetric (county) method were in good agreement with soils having an exchangeable potassium content of 320 pounds/acre or less, but the turbidimetric method gave significantly lower exchangeable potassium values in regard to soils containing more than 320 pounds/acre.
2. Fluctuations in soil exchangeable potassium levels occurred during storage suggesting the occurrence of insidious variations in soil moisture content. This indicates soil samples for critical exchangeable potassium determinations should be protected from variations in moisture content.
3. Coefficients of variation showed the turbidimetric method is approximately one-half as reliable as the flame photometric method. Average coefficients of variation obtained for the two methods were 4.107% and 2.182%, respectively.
4. The percentage error in measurement of sodium cobaltinitrite powder (used in the turbidimetric method) was imparted to the determined exchangeable potassium value in a ratio of 1.5:1, using a standardization solution of 45ppm potassium and a sodium cobaltinitrite weight range of .090-.110g., e.g. a 10% measurement error resulted in approximately a $6\frac{2}{3}$'s % error in the determined pounds of exchangeable potassium per acre.

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LITERATURE CITED

1. Bates, T. E. and A. D. Scott
Control of potassium release and reversion associated with changes in soil moisture. Soil Sci. Soc. Amer. Proc. 33: 566-568. 1969.
2. Bear, F. E.
Historical introduction. In Diagnostic techniques for soils and crops. The American Potash Institute. Washington D.C. p. ix-xxiii. 1948.
3. Black, C. A.
Soil-plant relationships. John Wiley and Sons, Inc., New York. 332 p. 1957.
4. Bohannon, R. A.
The effect of drying on exchangeable potassium in soils from Illinois and Kansas. Ph.D. Thesis. Univ. of Illinois. 118 p. Univ. Microfilms. Ann Arbor, Mich. (Mic. 58-4000). 1957.
5. Bolt, G. H., M. E. Sumner, and A. Kamphorst
A study of the equilibria between three categories of potassium in an illitic soil. Soil Sci. Soc. Amer. Proc. 27: 294-299. 1963.
6. Dowdy, R. H. and T. B. Hutcheson, Jr.
Effect of exchangeable potassium level and drying on release and fixation of potassium by soils as related to clay mineralogy. Soil Sci. Soc. Amer. Proc. 27: 31-34. 1963.
7. Garmen, W. L.
Potassium release characteristics of several soils from Ohio and New York. Soil Sci. Soc. Amer. Proc. 21: 52-58. 1957.
8. Gieseking, J. E. and H. Jenny
Behavior of polyvalent cations in base exchange. Soil Sci. 42: 273-280. 1936.
9. Golden, L. E.
The effect of soil moisture content, temperature of extractant and time of sampling on phosphorus and potassium extractable from soils cropped to sugar cane in Louisiana. Louisiana State University Bull. 621. 27 p. 1967.
10. Hanway, J. J. and A. D. Scott
Soil potassium-moisture relations: II. Profile distribution of exchangeable K in Iowa soils as influenced by drying and rewetting. Soil Sci. Soc. Amer. Proc. 21: 501-504. 1957.

11. Jackson, M. L.
Soil chemical analysis. Prentice-Hall, Inc., Englewood Cliffs,
N. J. 498 p. 1958.
12. Luebs, R. E., G. Stanford, and A. D. Scott
Relation of available potassium to soil moisture. Soil Sci.
Soc. Amer. Proc. 20: 45-50. 1956.
13. McIntosh, J. L.
Bray and Morgan soil extractants modified for testing acid soils
from different parent materials. Agron. J. 61: 259-265. 1969.
14. Merwin, H. D. and M. Peech
Exchangeability of soil potassium in the sand, silt, and clay
fractions as influenced by the nature of the complementary exchange-
able cation. Soil Sci. Soc. Amer. Proc. 15: 125-128. 1950.
15. Millar, C. E.
Soil fertility. John Wiley and Sons, Inc., New York. 436 p. 1955.
16. Olson, R. V.
A turbidimetric potassium determination affected little by
temperature. Soil Sci. Soc. Amer. Proc. 17: 20-22. 1953.
17. Peech, M. and L. English
Rapid microchemical soil tests. Soil Sci. 57: 167-195. 1945.
18. Reitemeier, R. F.
Soil potassium. In A. G. Norman (ed.) Advances in Agronomy.
Academic Press, Inc., New York. 3: 113-164. 1951.
19. Rich, C. I.
Effect of cation size and pH on potassium exchange in Nason soil.
Soil Sci. 98: 100-106. 1964.
20. Rich, C. I. and W. R. Black
Potassium exchange as affected by cation size, pH, and mineral
structure. Soil Sci. 97: 384-390. 1963.
21. Scott, A. D. and T. E. Bates
Changes in exchangeable potassium observed on drying soils after
treatment with organic compounds: II. Reversion. Soil Sci. Soc.
Amer. Proc. 31: 481-485. 1967.
22. Scott, T. W. and F. W. Smith
Effect of drying upon the availability of potassium in Parsons
silt loam surface soil and subsoil. Agron. J. 49: 377-380. 1957.
23. Wiklander, L.
Forms of potassium in the soil. Potassium Symp. Ann. Meeting
Intern. Potash Inst. p. 110-121. 1954.

24. Wiklander, L.
Cation and anion exchange phenomena. p. 163-205. In Bear,
F. E. (ed.) Chemistry of the soil. 2nd ed. Reinhold Publishing
Corp., New York. 515 p. 1964.
25. Williams, D. E. and H. Jenny
The replacement of nonexchangeable potassium by various acids and
salts. Soil Sci. Soc. Amer. Proc. 16: 216-221. 1952.

APPENDIX

Table 1. Soil exchangeable potassium levels, as determined by the flame photometric method and turbidimetric method, and effect of storage time on soil exchangeable potassium content.

| County | Sample Number | Pounds Exchangeable Potassium Per Acre | | | | |
|--------|---------------|--|---------|----------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Barton | 1 | 1462 | | | 1055 | 1229 |
| | 2 | 1167 | | | 818 | 989 |
| | 3 | 653 | | 435 | 446 | 406 |
| | 4 | 886 | | 616 | 563 | 580 |
| | 5 | 488 | | 354 | 358 | 318 |
| | 6 | 504 | 450 | 474 | 366 | 348 |
| | 7 | 1130 | | | 801 | 860 |
| | 8 | 612 | | | 337 | 351 |
| | 9 | 783 | | | 531 | 579 |
| | 10 | 978 | | 780 | 714 | 746 |
| | 11 | 398 | | 324 | 246 | 281 |
| | 12 | 538 | 477 | 411 | 318 | 362 |
| | 13 | 484 | | | 305 | 324 |
| | 14 | 689 | | | 480 | 540 |
| | 15 | 837 | | | 582 | 660 |
| | 16 | 957 | | | 680 | 786 |
| | 17 | 693 | | | 470 | 489 |
| | 18 | 827 | | | 590 | 644 |
| | 19 | 614 | | | 410 | 413 |
| | 20 | 849 | | | 517 | 557 |
| | 21 | 827 | | 623 | 575 | 636 |

Table 1. (Continued)

| County | Sample Number | Pounds Exchangeable Potassium Per Acre | | | | |
|--------------|------------------|--|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Barton | 22 | 1256 | | | 911 | 1038 |
| Bourbon | 1 | 242 | 189 | 174 | 170 | 179 |
| | 2 | 203 | | | 126 | 121 |
| | 3 | 197 | 148 | 176 | 170 | 189 |
| | 4 | 345 | | | 182 | 189 |
| | 5 | 215 | 172 | 154 | 145 | 158 |
| | 6 | 145 | 120 | 113 | 100 | 93 |
| | 7 | 318 | | 268 | 206 | 214 |
| | 8 | 203 | | | 145 | 152 |
| | 9 | 341 | | | 251 | 251 |
| | 10 | 316 | | 242 | 181 | 177 |
| | 11 | 472 | 428 | 324 | 307 | 325 |
| Chautauqua A | 1 | 108 | | | 98 | 76 |
| | 2 | 272 | | | 198 | 201 |
| | 3 | 353 | | 255 | 198 | 219 |
| | 4 | 463 | | | 373 | 408 |
| | 5 | 437 | | 342 | 285 | 316 |
| | 6 | 441 | | | | 288 |
| | 7 | | | | 800 | |
| | 8 | 415 | | 350 | 291 | 294 |
| | 9 | 1160 | | | 861 | 932 |

Table 1. (Continued)

| County | Sample Number | Pounds Exchangeable Potassium Per Acre | | | | |
|--------------|------------------|--|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Chautauqua A | 10 | 459 | | | 287 | 276 |
| | 11 | 732 | | | 534 | 598 |
| | 12 | 815 | | | 614 | 681 |
| | 13 | 1491 | | | 1212 | |
| | 14 | 1451 | | | 1211 | |
| Chautauqua B | 1 | 254 | | | | 173 |
| | 2 | 264 | | | | 198 |
| | 3 | 293 | | | | |
| | 4 | 226 | | | | 157 |
| | 5 | 334 | | | | 213 |
| | 6 | 233 | | | | 129 |
| | 7 | 276 | | | | 147 |
| | 8 | 254 | | | | 184 |
| | 9 | 362 | | | | 249 |
| | 10 | 236 | | | | 158 |
| | 11 | 412 | | | | 340 |
| | 12 | 262 | | | | 203 |
| | 13 | 154 | | | | 93 |
| | 14 | 258 | | | | 165 |
| | 15 | 271 | | | | 192 |
| | 16 | 270 | | | | 185 |

Samples 17 through 19, inclusive, not included in study.

Table 1. (Continued)

| County | Sample Number | Pounds Exchangeable Potassium Per Acre | | | | |
|--------------|------------------|--|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Chautauqua B | 20 | 406 | | | | 256 |
| | 21 | 387 | | | | 246 |
| | 22 | 288 | | | | 176 |
| | 23 | 284 | | | | 189 |
| | 24 | 188 | | | | 136 |
| | 25 | 338 | | | | 204 |
| | 26 | 470 | | | | 323 |
| | 27 | 272 | | | | 185 |
| Cherokee | 1 | 242 | | | | 235 |
| | 2 | 197 | | | 149 | |
| | 3 | 138 | 105 | 111 | 105 | 107 |
| | 4 | 483 | | | 380 | 434 |
| | 5 | 139 | 105 | 114 | 104 | 105 |
| | 6 | 147 | 120 | 128 | 102 | 107 |
| | 7 | 171 | 124 | 130 | 121 | 140 |
| | 8 | 194 | | | 139 | 147 |
| | 9 | 1523 | 1063 | | 1182 | |
| | 10 | 568 | | | 484 | 511 |
| Coffey | 1 | 178 | 148 | 151 | 146 | 160 |
| | 2 | 269 | 229 | 212 | 210 | 207 |

Table 1. (Continued)

| County | Sample Number | Pounds Exchangeable Potassium Per Acre | | | | |
|---------|------------------|--|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Edwards | 1 | 642 | | | 514 | 603 |
| | 2 | 436 | 314 | 357 | 328 | 362 |
| | 3 | 911 | | | 633 | 746 |
| | 4 | 641 | 489 | 522 | 492 | 510 |
| | 5 | 916 | | | 591 | 754 |
| | 6 | 405 | | | 363 | 306 |
| | 7 | 303 | 225 | 300 | 276 | 320 |
| | 8 | 281 | 213 | 262 | 245 | 255 |
| | 9 | 701 | | | 536 | 611 |
| | 10 | 198 | 163 | 233 | 214 | 222 |
| Ellis | 1 | 737 | 588 | 520 | 477 | |
| | 2 | 1201 | 892 | 845 | 727 | |
| | 3 | 1103 | | | 706 | |
| | 4 | 978 | | | 606 | |
| Finney | 1 | 1417 | | | 837 | |
| | 2 | 2584 | | | 1791 | |
| | 3 | 2124 | | | 1497 | |
| | 4 | 1950 | | | 1419 | |
| | 5 | 1068 | | | 648 | |
| | 6 | 1846 | | | 1212 | |
| | 7 | 1979 | | | 1461 | |

Table 1. (Continued)

| County | Sample Number | Pounds Exchangeable Potassium Per Acre | | | | |
|-----------|------------------|--|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Finney | 8 | 1974 | | | 1374 | |
| | 9 | 2145 | | | 1605 | |
| | 10 | 317 | | | | |
| | 11 | 303 | | | 264 | |
| | 12 | 683 | 547 | | 492 | |
| Jefferson | 1 | 286 | 257 | 239 | 192 | 198 |
| | 2 | 378 | 335 | 258 | 259 | 265 |
| | 3 | 634 | 476 | 394 | 437 | 426 |
| | 4 | 442 | 381 | 383 | 392 | 366 |
| | 5 | 518 | | | 323 | 353 |
| | 6 | 402 | | | 371 | 381 |
| | 7 | 258 | | | 160 | 182 |
| | 8 | 244 | | | 190 | 213 |
| Marshall | 1 | 771 | | | 496 | 531 |
| | 2 | 771 | | | 479 | 518 |
| | 3 | 298 | | | 192 | 202 |
| | 4 | 457 | | | 319 | 322 |
| | 5 | 609 | | | 407 | 456 |
| | 6 | 325 | | | 211 | 244 |
| | 7 | 959 | | | 617 | 702 |
| | 8 | 1614 | | | 1130 | |

Table 1. (Continued)

| County | Sample Number | Pounds Exchangeable Potassium Per Acre | | | | |
|----------|------------------|--|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Marshall | 9 | 1019 | | | 719 | |
| | 10 | 644 | | | 429 | |
| Neosho | 1 | 304 | | 242 | 141 | 173 |
| | 2 | 290 | 274 | 252 | 176 | 184 |
| | 3 | 235 | 263 | 194 | 142 | 116 |
| | 4 | 215 | 183 | 168 | | 123 |
| | 5 | 182 | 129 | 136 | 135 | 121 |
| | 6 | 186 | | | 112 | 102 |
| | 7 | | | | 81 | 78 |
| | 8 | 289 | 392 | | 216 | 212 |
| | 9 | 591 | | | 424 | |
| Saline | 1 | 625 | | | 469 | 510 |
| | 2 | 714 | | | 601 | 639 |
| | 3 | 686 | | | 581 | 635 |
| | 4 | 600 | | | 446 | 468 |
| | 5 | 742 | | | 581 | 668 |
| | 6 | 666 | | | | 564 |
| | 7 | 706 | | | 522 | 546 |
| | 8 | 638 | | | 461 | 485 |
| | 9 | 626 | | | 490 | 528 |

Table 1. (Continued)

| County | Sample Number | Pounds Exchangeable Potassium Per Acre | | | | |
|--------|------------------|--|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Summer | 1 | 452 | 453 | 352 | 308 | 345 |
| | 2 | 531 | 454 | 393 | 369 | 398 |
| | 3 | 855 | | | 615 | 650 |
| | 4 | 498 | | | 294 | 273 |
| | 5 | 476 | 458 | 360 | 326 | 348 |
| | 6 | 240 | | | 207 | 189 |
| | 7 | 482 | | | 332 | 355 |
| | 8 | 690 | | | 539 | 559 |
| | 9 | 474 | 372 | 305 | 271 | 294 |
| | 10 | 511 | | | 320 | 360 |
| | 11 | 373 | | | 205 | 199 |
| | 12 | 658 | | | 490 | 567 |
| | 13 | 490 | | 302 | 266 | 282 |
| Thomas | 1 | 1367 | | | 1102 | |
| | 2 | 2753 | | | | |
| | 3 | 2115 | | | 1623 | |
| | 4 | 2154 | | | 1674 | |
| | 5 | 2234 | | | 1653 | |
| | 6 | 1400 | | | 1026 | |
| | 7 | 2063 | | | 1506 | |
| | 8 | 1635 | | | 1206 | |
| | 9 | 1394 | | | 921 | |
| | 10 | 1906 | | | 1386 | |

Table 1. (Concluded)

| County | Sample Number | Pounds Exchangeable Potassium Per Acre | | | | |
|---------|------------------|--|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Woodson | 1 | 198 | 160 | 133 | 120 | 136 |
| | 2 | 285 | 231 | 245 | 227 | 222 |
| | 3 | 221 | 163 | | 161 | 154 |
| | 4 | 263 | 223 | 200 | 173 | 171 |
| | 5 | 236 | | | 155 | 154 |
| | 6 | 277 | | | | 200 |
| | 7 | 190 | | | 123 | 119 |
| | 8 | 197 | | | 135 | 144 |
| | 9 | 290 | | | 222 | |
| | 10 | 256 | | | 203 | |

Table 2. Coefficients of variation of soil exchangeable potassium values, as determined by the flame photometric method and turbidimetric method, and effect of storage time on soil exchangeable potassium content.

| County | Sample Number | Coefficient of Variation (%) | | | | |
|--------|---------------|------------------------------|---------|----------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Barton | 1 | 0.193 | | | 2.615 | 16.718 |
| | 2 | 4.828 | | | 6.743 | 20.374 |
| | 3 | 4.790 | | 0.000 | 0.000 | 4.877 |
| | 4 | 0.319 | | 1.607 | 2.261 | 4.877 |
| | 5 | 5.749 | | 2.397 | 2.571 | 2.668 |
| | 6 | 5.568 | 0.000 | 16.111 | 2.515 | 4.877 |
| | 7 | 1.752 | | | 0.000 | 1.973 |
| | 8 | 0.000 | | | 8.195 | 4.835 |
| | 9 | 0.000 | | | 0.799 | 2.198 |
| | 10 | 0.868 | | 0.000 | 11.290 | 4.837 |
| | 11 | 0.534 | | 3.491 | 6.624 | 5.536 |
| | 12 | 2.103 | 1.488 | 1.550 | 2.668 | 0.781 |
| | 13 | 1.169 | | | 1.391 | 1.746 |
| | 14 | 2.157 | | | 0.000 | 3.143 |
| | 15 | 0.000 | | | 2.916 | 0.000 |
| | 16 | 0.443 | | | 4.683 | 2.699 |
| | 17 | 1.224 | | | 4.970 | 0.868 |
| | 18 | 0.770 | | | 1.080 | 4.945 |
| | 19 | 1.729 | | | 8.806 | 6.685 |
| | 20 | 0.000 | | | 2.452 | 1.144 |
| | 21 | 0.770 | | 0.000 | 4.800 | 5.337 |

Table 2. (Continued)

| County | Sample Number | Coefficient of Variation (%) | | | | |
|--------------|------------------|------------------------------|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Barton | 22 | 1.183 | | | 2.097 | .409 |
| Bourbon | 1 | 0.584 | 1.496 | 4.876 | 4.991 | 2.370 |
| | 2 | 2.787 | | | 2.244 | 0.000 |
| | 3 | 1.799 | 3.821 | 0.000 | 4.991 | 3.376 |
| | 4 | 2.660 | | | 8.547 | 1.125 |
| | 5 | 0.989 | 1.644 | 8.265 | 6.361 | 1.790 |
| | 6 | 1.950 | 2.958 | 3.142 | 10.205 | 0.000 |
| | 7 | 0.000 | | 0.000 | 4.119 | 6.608 |
| | 8 | 0.697 | | | 0.000 | 7.443 |
| | 9 | 0.829 | | | 1.690 | 1.690 |
| | 10 | 1.121 | | 3.506 | 3.526 | 0.799 |
| | 11 | 1.813 | 0.491 | 2.603 | 3.461 | 5.657 |
| Chautauqua A | 1 | 9.876 | | | 3.627 | 1.861 |
| | 2 | 0.000 | | | 10.382 | 0.703 |
| | 3 | 2.578 | | 7.209 | 5.907 | 0.646 |
| | 4 | 2.582 | | | 6.446 | 6.239 |
| | 5 | 0.810 | | 1.240 | 0.000 | 0.000 |
| | 6 | 0.000 | | | | 3.928 |
| | 7 | | | | 1.857 | |
| | 8 | 0.000 | | 7.272 | 12.241 | 0.962 |
| | 9 | 1.281 | | | 7.912 | 17.706 |

Table 2. (Continued)

| County | Sample Number | Coefficient of Variation (%) | | | | |
|--------------|------------------|------------------------------|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Chautauqua A | 10 | 16.810 | | | 10.569 | 0.000 |
| | 11 | 2.318 | | | 6.578 | 13.865 |
| | 12 | 1.302 | | | 10.027 | 20.457 |
| | 13 | 1.992 | | | 11.202 | |
| | 14 | 2.779 | | | 7.769 | |
| Chautauqua B | 1 | 1.953 | | | | 7.357 |
| | 2 | 0.536 | | | | 1.428 |
| | 3 | 3.356 | | | | |
| | 4 | 3.061 | | | | 6.305 |
| | 5 | 3.572 | | | | 5.976 |
| | 6 | 2.129 | | | | 8.254 |
| | 7 | 0.770 | | | | 2.886 |
| | 8 | 0.000 | | | | 2.698 |
| | 9 | 1.172 | | | | 0.568 |
| | 10 | 2.702 | | | | 1.790 |
| | 11 | 1.203 | | | | 4.159 |
| | 12 | 1.619 | | | | 0.697 |
| | 13 | 0.000 | | | | 5.351 |
| | 14 | 1.922 | | | | 4.285 |
| | 15 | 3.131 | | | | 3.323 |
| | 16 | 2.361 | | | | 3.822 |

Samples 17 through 19, inclusive, not included in study.

Table 2. (Continued)

| County | Sample Number | Coefficient of Variation (%) | | | | |
|--------------|------------------|------------------------------|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Chautauqua B | 20 | 0.697 | | | | 0.830 |
| | 21 | 2.716 | | | | 1.440 |
| | 22 | 2.214 | | | | 0.000 |
| | 23 | 2.715 | | | | 4.466 |
| | 24 | 3.009 | | | | 0.000 |
| | 25 | 0.628 | | | | 0.000 |
| | 26 | 0.301 | | | | 0.000 |
| | 27 | 1.302 | | | | 3.822 |
| Cherokee | 1 | 0.875 | | | | 9.348 |
| | 2 | 1.799 | | | 8.542 | |
| | 3 | 1.543 | 6.088 | 1.274 | 0.646 | 4.648 |
| | 4 | 0.440 | | | 0.937 | 0.000 |
| | 5 | 0.000 | 6.088 | 1.869 | 0.000 | 0.000 |
| | 6 | 0.000 | 1.902 | 13.864 | 0.000 | 4.648 |
| | 7 | 0.000 | 7.442 | 2.175 | 1.169 | 4.041 |
| | 8 | 0.000 | | | 4.070 | 4.810 |
| | 9 | 1.631 | 19.632 | | 3.111 | |
| | 10 | 3.056 | | | 1.753 | 0.830 |
| Coffey | 1 | 3.950 | 0.000 | 5.168 | 13.561 | 7.919 |
| | 2 | 4.679 | 0.000 | 0.000 | 2.050 | 2.050 |

Table 2. (Continued)

| County | Sample Number | Coefficient of Variation (%) | | | | |
|---------|------------------|------------------------------|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Edwards | 1 | 0.000 | | | 0.000 | 5.893 |
| | 2 | 10.380 | 0.000 | 5.150 | 1.725 | 0.781 |
| | 3 | 0.704 | | | 7.373 | 3.130 |
| | 4 | 3.947 | 1.735 | 1.664 | 3.449 | 4.991 |
| | 5 | 7.169 | | | 23.097 | 4.877 |
| | 6 | 0.175 | | | 18.248 | 4.159 |
| | 7 | 3.039 | 2.513 | 3.771 | 0.000 | 3.320 |
| | 8 | 6.923 | 2.994 | 7.301 | 0.000 | 7.920 |
| | 9 | 1.514 | | | 3.565 | 2.432 |
| | 10 | 5.832 | 2.175 | 1.820 | 1.321 | 1.274 |
| Ellis | 1 | 5.505 | 0.000 | 9.664 | 0.890 | |
| | 2 | 0.119 | 1.426 | 16.662 | 0.000 | |
| | 3 | 2.834 | | | 2.604 | |
| | 4 | 2.387 | | | 0.000 | |
| Finney | 1 | 1.303 | | | 5.576 | |
| | 2 | 2.960 | | | 1.658 | |
| | 3 | 4.394 | | | 5.952 | |
| | 4 | 0.435 | | | 1.495 | |
| | 5 | 0.794 | | | 0.000 | |
| | 6 | 1.377 | | | 4.901 | |
| | 7 | 4.077 | | | 2.614 | |

Table 2. (Continued)

| County | Sample Number | Coefficient of Variation (%) | | | | |
|-----------|---------------|------------------------------|---------|----------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Finney | 8 | 10.058 | | | 4.323 | |
| | 9 | 0.593 | | | 1.322 | |
| | 10 | 5.317 | | | | |
| | 11 | 2.090 | | | 16.499 | |
| | 12 | 2.166 | 0.000 | | 3.449 | |
| Jefferson | 1 | 1.239 | 3.583 | 5.326 | 1.108 | 1.428 |
| | 2 | 0.374 | 1.063 | 5.481 | 0.821 | 5.870 |
| | 3 | 2.017 | 0.000 | 4.133 | 8.090 | 0.000 |
| | 4 | 1.441 | 1.855 | 13.864 | 10.075 | 2.515 |
| | 5 | 2.379 | | | 1.314 | 4.614 |
| | 6 | 0.703 | | | 7.243 | 3.341 |
| | 7 | 0.548 | | | 7.537 | 1.554 |
| | 8 | 1.452 | | | 18.054 | 1.992 |
| Marshall | 1 | 1.630 | | | 6.843 | 0.799 |
| | 2 | 0.000 | | | 3.248 | 2.730 |
| | 3 | 1.898 | | | 4.800 | 1.400 |
| | 4 | 0.928 | | | 7.537 | 2.635 |
| | 5 | 2.090 | | | 3.822 | 4.962 |
| | 6 | 0.435 | | | 3.351 | 2.318 |
| | 7 | 2.189 | | | 2.060 | 3.626 |
| | 8 | 12.386 | | | 1.332 | |

Table 2. (Continued)

| County | Sample Number | Coefficient of Variation (%) | | | | |
|----------|------------------|------------------------------|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Marshall | 9 | 1.458 | | | 5.019 | |
| | 10 | 2.189 | | | 0.000 | |
| Neosho | 1 | 0.000 | | 3.506 | 17.051 | 2.453 |
| | 2 | 0.975 | 6.633 | 8.716 | 1.790 | 0.000 |
| | 3 | 2.111 | 6.734 | 10.206 | 1.554 | 0.000 |
| | 4 | 0.989 | 4.982 | 3.799 | | 2.299 |
| | 5 | 0.000 | 10.100 | 4.160 | 29.423 | 0.000 |
| | 6 | 1.143 | | | 9.753 | 4.877 |
| | 7 | | | | 2.737 | 3.626 |
| | 8 | 0.489 | 8.024 | | 3.304 | 5.337 |
| | 9 | 0.834 | | | 0.000 | |
| Saline | 1 | 1.472 | | | 8.456 | 1.109 |
| | 2 | 3.961 | | | 0.706 | 1.549 |
| | 3 | 0.000 | | | 2.191 | 4.231 |
| | 4 | 0.476 | | | 6.976 | 3.626 |
| | 5 | 0.000 | | | 10.440 | 0.000 |
| | 6 | 1.274 | | | | 3.009 |
| | 7 | 1.303 | | | 3.793 | 1.554 |
| | 8 | 0.443 | | | 7.056 | 1.458 |
| | 9 | 0.000 | | | 1.732 | 0.000 |

Table 2. (Continued)

| County | Sample Number | Coefficient of Variation (%) | | | | |
|--------|------------------|------------------------------|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| Sumner | 1 | 1.732 | 1.406 | 3.214 | 5.510 | 4.509 |
| | 2 | 0.133 | 14.328 | 4.678 | 6.515 | 0.711 |
| | 3 | 0.746 | | | 5.749 | 2.176 |
| | 4 | 0.711 | | | 3.848 | 3.626 |
| | 5 | 1.338 | 8.195 | 0.000 | 0.867 | 6.502 |
| | 6 | 2.357 | | | 4.782 | 2.245 |
| | 7 | 0.147 | | | 1.704 | 3.585 |
| | 8 | 1.845 | | | 3.411 | 2.793 |
| | 9 | 0.449 | 8.945 | 6.955 | 1.589 | 2.886 |
| | 10 | 2.227 | | | 1.768 | 3.143 |
| | 11 | 0.758 | | | 3.449 | 0.711 |
| | 12 | 3.200 | | | 1.732 | 5.238 |
| | 13 | 3.046 | | 0.000 | 1.063 | 1.003 |
| Thomas | 1 | 8.212 | | | 0.847 | |
| | 2 | 4.542 | | | | |
| | 3 | 1.404 | | | 2.875 | |
| | 4 | 4.425 | | | 1.521 | |
| | 5 | 0.386 | | | 5.390 | |
| | 6 | 0.000 | | | 2.481 | |
| | 7 | 1.012 | | | 1.690 | |
| | 8 | 1.302 | | | 7.739 | |
| | 9 | 3.657 | | | 2.303 | |

Table 2. (Concluded)

| County | Sample Number | Coefficient of Variation (%) | | | | |
|---------|------------------|------------------------------|---------|-------------------------|----------|---------|
| | | Flame Photometric Method | | Turbidimetric Method | | |
| | | June-July/'65 | Apr/'66 | Apr/'66 | Sept/'65 | Aug/'65 |
| | | | | | | |
| Thomas | 10 | 0.222 | | | 0.000 | |
| Woodson | 1 | 2.857 | 0.000 | 13.341 | 0.000 | 4.697 |
| | 2 | 0.746 | 1.224 | 5.195 | 4.683 | 1.274 |
| | 3 | 1.280 | 1.734 | | 2.635 | 1.836 |
| | 4 | 3.226 | 1.268 | 11.691 | 8.801 | 9.097 |
| | 5 | 1.501 | | | 3.204 | 9.183 |
| | 6 | 3.523 | | | | 2.829 |
| | 7 | 0.000 | | | 3.450 | 2.984 |
| | 8 | 1.799 | | | 3.143 | 0.000 |
| | 9 | 0.975 | | | 6.065 | |
| | 10 | 0.830 | | | 3.483 | |

AN EVALUATION OF TWO CHEMICAL METHODS FOR
THE DETERMINATION OF POTASSIUM IN SOILS

by

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B. S., Kansas State University, 1965

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ABSTRACT

The purpose of this investigation was to obtain more knowledge about the two chemical methods currently used in Kansas to determine the exchangeable potassium content of soils. Doubt existed as to whether the turbidimetric solid cobaltinitrite method used in county agricultural agent laboratories was in acceptable agreement with the rapid flame emission spectrophotometer method used in the Kansas State University soil testing laboratory.

The exchangeable potassium content of 173 soil samples collected from selected counties in Kansas was determined by both above-mentioned chemical methods. The findings of this study are summarized briefly as follows:

1. Exchangeable potassium determinations by the flame photometric (state) method and the turbidimetric (county) method were in good agreement with soils having an exchangeable potassium content of 320 pounds/acre or less, but the turbidimetric method gave significantly lower exchangeable potassium values in regard to soils containing more than 320 pounds/acre.
2. Fluctuations in soil exchangeable potassium levels occurred during storage suggesting the occurrence of insidious variations in soil moisture content. This indicates soil samples for critical exchangeable potassium determinations should be protected from variations in moisture content.
3. Coefficients of variation showed the turbidimetric method is approximately one-half as precise as the flame photometric method. Average coefficients of variation obtained for the two methods

were 4.107% and 2.182%, respectively.

4. The percentage error in measurement of sodium cobaltinitrite powder (used in the turbidimetric method) was imparted to the determined exchangeable potassium value in a ratio of 1.5:1, using a standardization solution of 45ppm potassium and a sodium cobaltinitrite weight range of .090-.110g., e.g. a 10% measurement error resulted in, approximately, a 6.7% error in the determined pounds of exchangeable potassium per acre.