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Application of Ion Exchange to Flame Spectrophotometry & Determination of Potassium in Fertilizers

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Report on Department of Agricultural Chemistry
Research Project 132, "Analytical
Services"

Application of Ion Exchange to Flame Spectrophotometry

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Determination of Potassium in Fertilizers

In previous work (9, 10, 11) on flame photometric determination of potassium in commercial fertilizers at the Missouri Station, the ion exchange resin Amberlite IR-4B,* in the chloride form, was used to remove interfering anions prior to flame analysis. Reference standards were prepared from reagent grade KCl. Due to the NH_4Cl effect (Figures 1 and 2) the results obtained with this procedure were slightly higher than those obtained on the same samples by the official gravimetric method. The level of NH_4Cl in the aspirating solutions of the samples was about 2000 p.p.m., some being contributed by NH_4NO_3 and most of the remainder by $(NH_4)_2CO_3$. This reagent was substituted for $(NH_4)_2C_2O_4$ (official method) in the solution preparation step to precipitate the calcium and magnesium ions from a basic solution as insoluble carbonates. Upon contact of the sample aliquot with the resin IR-4B-Cl, all of the anions were exchanged for chloride ions on the resin. The concentration of NH_4Cl in the aspirating solutions of fertilizer samples containing a low percentage of K_2O was approximately 2000 p.p.m. However, with the recommended aliquots and dilutions for the higher percentage fertilizers, the concentration of NH_4Cl in the aspirating solution was considerably lower.

Attempts were made to correct for the NH_4Cl effect by adding it to the standards in amounts equivalent to those found in lower analysis fertilizer samples. Ammonium chloride also was added to the atomizing solutions of the higher percentage samples equal to the amounts added to the standards. The results of these experiments were not entirely satisfactory. Also, varying amounts of ammonia were volatilized during the initial boiling step; this made it more difficult to determine the exact amount of NH_4Cl remaining in the final solution. In cases where ammonia was lost, the maximum positive effect of NH_4Cl on the emission intensity of potassium had not been reached.

A series of analyses were made to determine the concentration of NH_4Cl in the aspirating solution of a group of different commercial fertilizer samples and the amount ranged from 1700 to 2600 p.p.m. Thus, the

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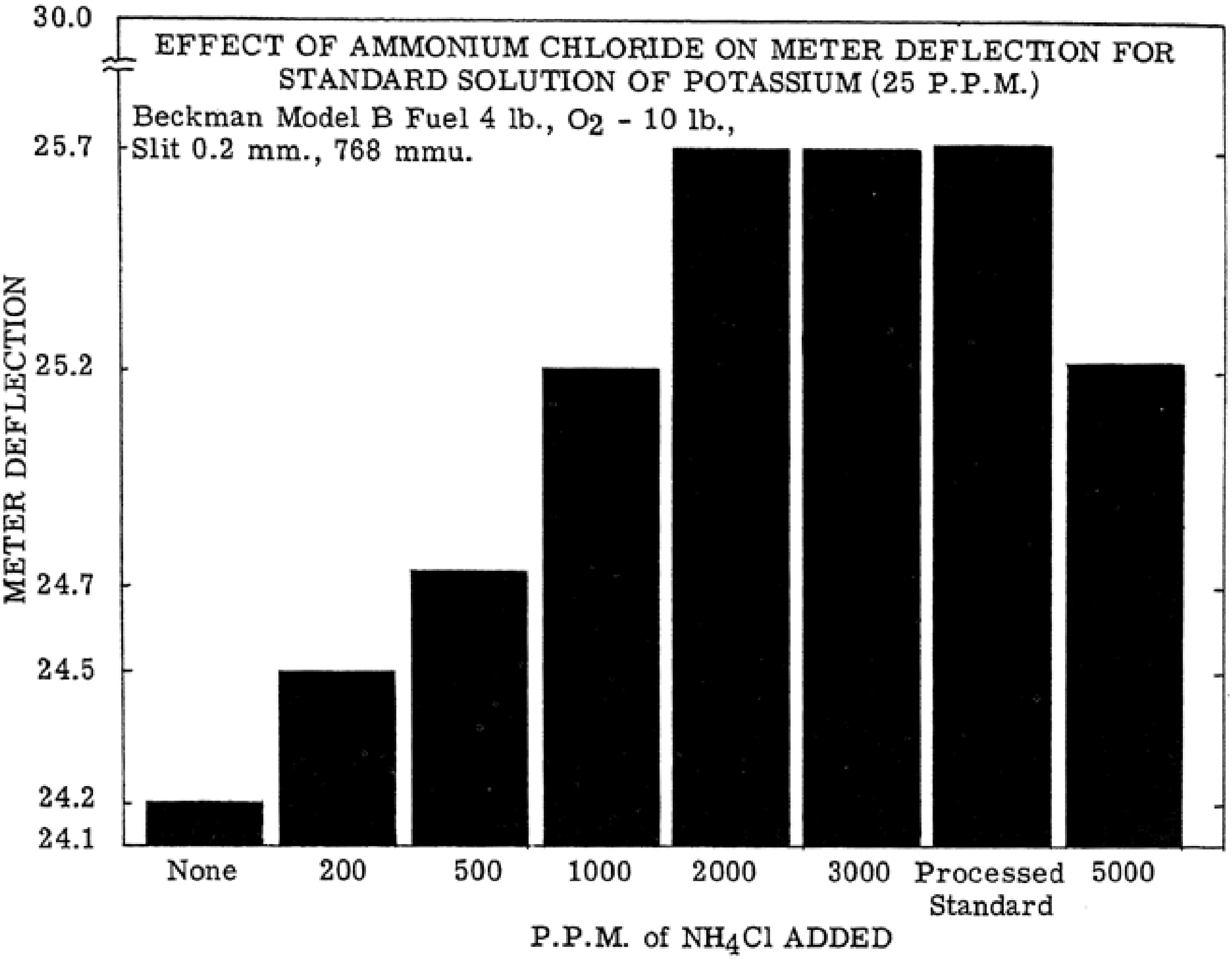
*Rohm and Haas Company, Philadelphia, Pennsylvania

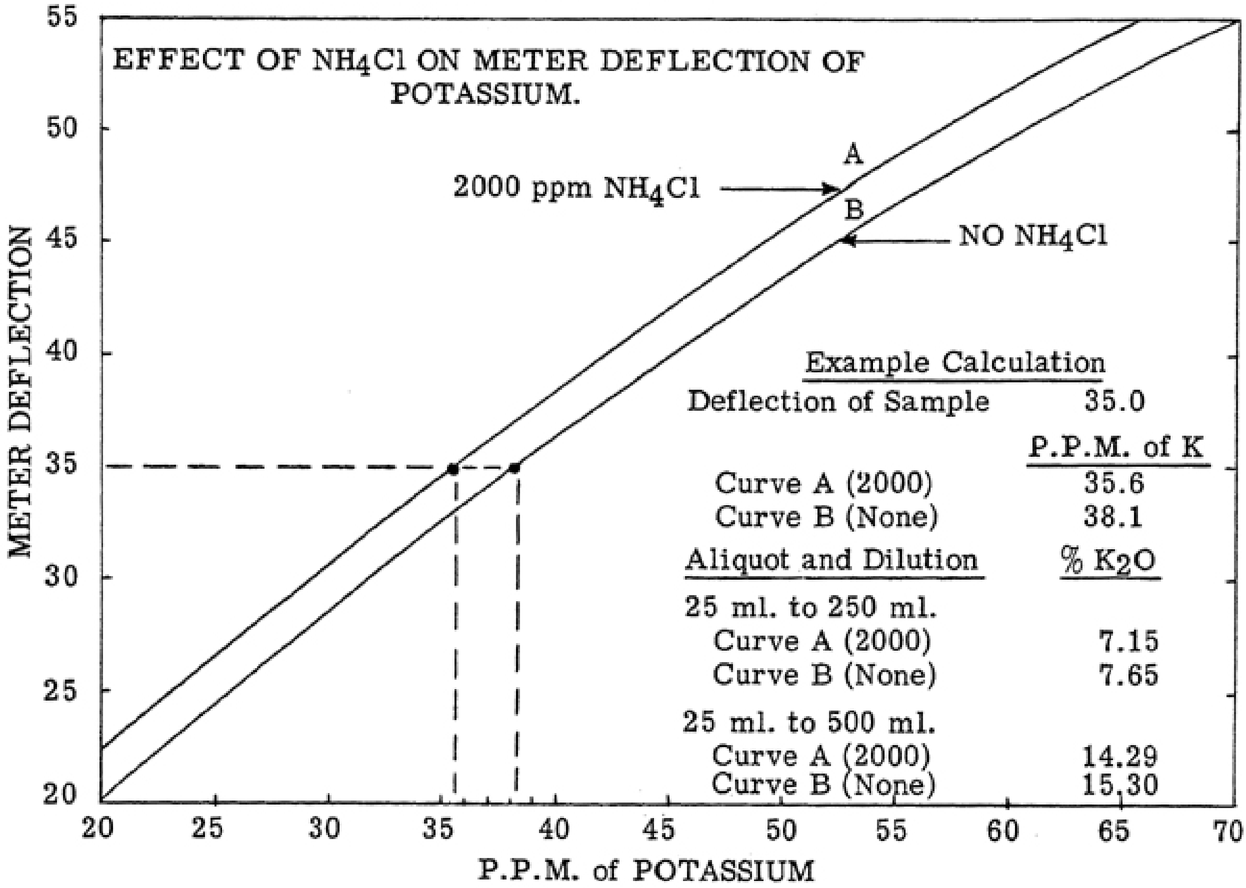
FIGURE 1



EFFECT OF AMMONIUM CHLORIDE ON METER DEFLECTION FOR STANDARD SOLUTION OF POTASSIUM (25 P.P.M.)

Beckman Model B Fuel 4 lb., O_2 - 10 lb., Slit 0.2 mm., 768 mmu.

FIGURE 2



EFFECT OF NH_4Cl ON METER DEFLECTION OF POTASSIUM.

Example Calculation

Deflection of Sample	35.0
	P.P.M. of K
Curve A (2000)	35.6
Curve B (None)	38.1
Aliquot and Dilution	% K_2O
25 ml. to 250 ml.	
Curve A (2000)	7.15
Curve B (None)	7.65
25 ml. to 500 ml.	
Curve A (2000)	14.29
Curve B (None)	15.30

meter deflection values obtained for samples not containing 2000 p.p.m. of NH_4Cl were different from the corresponding values of standards containing 2000 p.p.m. of NH_4Cl. Also, the presence of large amounts of NH_4Cl in the aspirating solution resulted in poorer atomizer performance.

During 1955 the flame results of approximately 1000 routine fertilizer samples determined as described above were compared with the A.O. A.C. official gravimetric data obtained on the same samples. In numerous cases the results did not agree within the laboratory analytical tolerances, and it was considered that a new approach was needed. Other studies concerning the effect of NH_4NO_3 on the emission intensity of potassium standards prepared from KNO_3 (Table 8) revealed that there was no enhancement or suppression of the potassium emission at levels as high as 2000 p.p.m. of added NO^-_3. This immediately solved the problem of the NH_4Cl effect. It was only necessary to place the weakly basic resin, Amberlite IR-4B, or any other acceptable resins (Table 32), in the NO^-_3 form and then exchange all of the different anions in the sample aliquot for the NO^-_3 ion on the resin. By this technique, the aspirating solution is changed into a single or binary system with a common anion. The interfering anions (PO^{---}_4, SO^{--}_4, Cl^-, etc.) are exchanged to the anion exchange resin and a common anion (NO^-_3) is substituted. Thus, the aspirating solution becomes a *simple system* and is compared to a *simple standard* containing only KNO_3, with no other added substances.

The early work on flame photometry dates back to the middle of the 19th century. The principle of quantitative spectral analysis, so brilliantly presented by Janssen in 1869, was successfully applied by Champion, Pellet and Grenier in 1873. These Frenchmen constructed a "spectronatrometre" consisting of a spectroscope provided with an attachment for the visual estimation of the intensity of sodium light and which permitted the determination of sodium in samples of plant ash to within 2 to 5% of the amount present. This was the first instrument for the determination of elements by flame spectrophotometry. Kirchoff and Bunsen (15) in 1860 used the flame as an excitation source; this was the flame of the Bunsen burner. However, it was not until the Swedish botanist, Lundegardh (16), described his work in 1928 that flame photometry was recognized as an important analytical tool. In Lundegardh's method, the atomized sample passed into a condensing chamber and thence into the base of an acetylene-air burner. The desired radiation was dispersed by means of a prism spectrograph and its intensity measured on a photographic plate. He mentioned the detection of nearly half the elements of the periodic system, but reported most on sodium, potassium, and the alkaline earths.

A comprehensive bibliography on flame photometry has been compiled by Mavrodineaun (18) and published in Applied Spectroscopy. Since this early work, many improvements have been made in flame photometry. New analytical techniques and applications of the method have been introduced, especially during the past ten years. Numerous studies have been conducted on the control and correction for interfering ions in the sample which affect the flame intensity of the determined ion. These investigations have emphasized the addition of radiation buffers, dilution, internal standard technique, the standard addition method, and the desired line-background correction method. Also, significant advances have been made in instrumentation and electronic circuitry. Vallee and Margoshes (24) of the Harvard Medical School built a multi-channel flame spectrometer with which they determined sodium, potassium, calcium, magnesium, and strontium, simultaneously. To date, their instrument is the ultimate in flame photometers and consists of an oxygen-hydrogen atomizer-burner with a large grating spectrograph, photocells and amplifiers, and associated power supplies and meters. At the ninth Annual Summer Symposium on "Rapid Methods of Analysis," Meloche (19), reviewed advancements in flame photometry. He discussed early methods, instruments, atomizer-burners, flame temperatures, interferences, and other points and included an extensive bibliography.

Rapid progress has been made in flame photometric methodology and application; however, much is yet to be done, and application of the principles of ion exchange and chelating agents to cleaning up the aspirating solution of complex samples, combined with new advances in instrumentation, should significantly increase the sensitivity, precision, and accuracy of flame analyses.

The objectives of this study were: To develop a simple, rapid, and accurate flame photometric method for the routine determination of potassium in commercial fertilizers; to clean up the sample aliquot with anion exchange resins and thus obviate the effects of interfering anions on the emission intensity of potassium; and to evaluate, quantitatively, under specified conditions, the magnitude of the interference on potassium produced by the common cations and anions found in fertilizers.

PART I
ANALYTICAL METHOD

Reagents:

Amberlite IR-4B-NO$_3$, a weakly basic anion exchange resin with a high capacity for phosphate, was used (Fisher Scientific Company). The resin was regenerated to the nitrate form in an ion exchange regenerating column (Figure 3). Other effective, acceptable resins are available; Duolite A-7, DeAcidite, Duolite A-41, Permutit-S, and Dowex 1.

Ammonium carbonate, analytical reagent, 5% solution.

Methyl red indicator, 0.2 gram of the indicator per 100 ml. of 95% ethyl alcohol.

Nitric acid, reagent grade, 1:5, 1:10, 5%.

Potassium nitrate, analytical reagent, recrystallized 3x.

Sodium hydroxide, 5% solution.

Apparatus:

A Beckman Model DU flame spectrophotometer with a red-sensitive phototube was used. The slit width was held at 0.095 mm. and the wave length used was 768 mμ. An oxygen-acetylene flame was used with an oxygen pressure of 10 pounds per square inch and an acetylene pressure of 4 pounds per square inch.

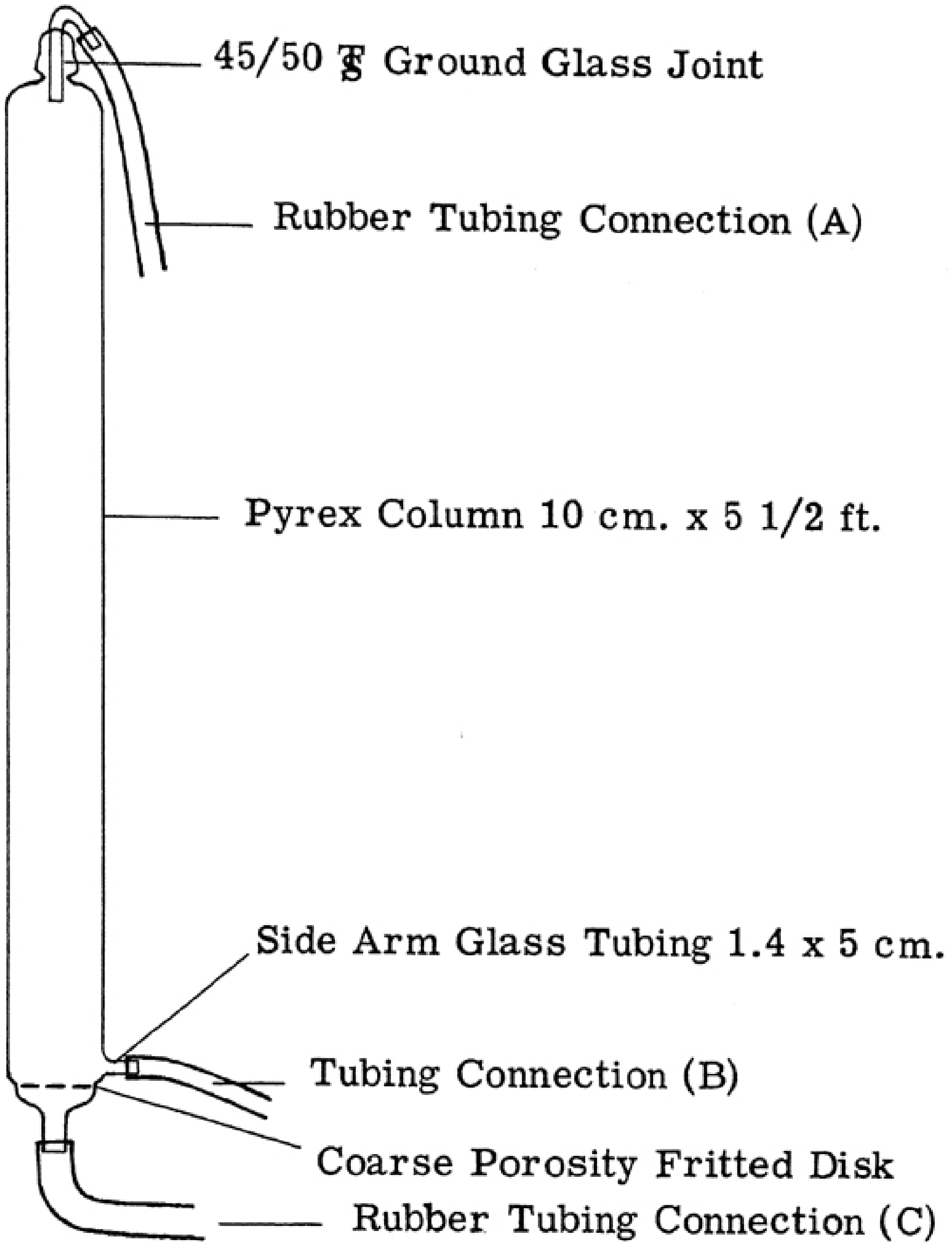
The graph paper used for preparing the standard curves was Keuffel and Esser, No. 282G, Standard Cross Section, 10 x 10 divisions to the inch, roll width 26 inches.

Ion exchange column and assembly as described under "Alternate Ion Exchange Column Method", Figures 5 and 5A.

An ion exchange regenerating column was constructed by attaching a 5 cm. length of tubing 1.4 cm. in diameter as a side arm directly above the fritted plate of a coarse porosity, 600 ml., Pyrex brand, Buchner funnel. The Buchner funnel was then attached to the end of a Pyrex glass tube with an outside wall diameter of 10.0 cm., and 5½ feet long. The top of the column was capped with a 45/50 standard taper, ground glass joint. A glass tube 1.2 cm. in diameter bent to an angle of 45° was sealed to the top of the ground glass joint for a rubber tubing connection (Figure 3).

Standard Volumetric and laboratory glassware.

FIGURE 3



ION EXCHANGE RESIN REGENERATING COLUMN

Procedure for Regeneration of Resin:

Ten-pound batches of resin were regenerated by first exhausting it with three separate treatments of 5% sodium hydroxide and back washing until all excess base was removed. The resin was then treated with three separate portions of 5% nitric acid. Finally, the resin was backwashed with distilled water to a pH of about 3.0. The resin slurry was drawn into the column (Figure 3) through the side arm (B) by attaching the top rubber tubing connection (A) to a filter pump and clamping off the lower rubber tubing connection (C). The regenerating solutions were introduced by drawing the solutions through the lower rubber tubing (C), and stirring of the resin-solution mixture was accomplished by drawing air through the lower rubber tubing connection (C). The regenerating solutions were removed by uncoupling the tubing connection from (A), which is connected to the filter pump, and allowing the solutions to drain through the fritted disk (C). Backwashing was accomplished by attaching a distilled water outlet to the lower rubber tubing connection (C). The resin was removed from the column by allowing it to drain through the side arm (B).

Procedure for Potassium in Fertilizers:

1. Weigh a 1.5058-gram sample of the fertilizer into a 250 ml. borosilicate glass volumetric flask.
2. Add approximately 100 ml. of distilled water.
3. Add 20 ml. of 5% ammonium carbonate.
4. Bring the solution to a boil and allow to boil for 15 minutes.
5. Remove from heat, allow to cool, dilute to the mark, mix and filter. (Use Whatman No. 12 folded filter paper or equivalent.)
6. Take aliquots as designated below and place them in a 300 ml. Phillips beaker or wide mouth Erlenmeyer flask, or proceed as described under "Alternate Column Method," page 14.

Estimated K_2O (%)	Aliquot (ml.)
0 to 24	25
25 to 63	20

7. Add 2 drops of methyl red indicator.
8. Adjust to a pH of approximately 5 with 1 to 10 nitric acid—acid side of methyl red.
9. Add 25 to 30 ml. of damp Amberlite IR-4B-NO_3 resin to ensure complete contact with the aliquot solution.
10. Shake continuously for 5 minutes or alternately for 15 minutes.
11. Filter directly into a volumetric flask. (Use Schleicher and Schuell No. 595 or any other equivalent high-speed, tough, filter paper.)

12. Use volumetric dilution flasks as designated below for the respective guarantees of K_2O given.

Sample Guarantee (%)	Volumetric flask (ml.)
0 to 12	250
13 to 30	500
31 to 63	1000

13. Wash the resin thoroughly using a series of 5 to 10 ml. increments of distilled water until the volumetric flasks are nearly full.
14. Dilute to the mark and mix thoroughly.
15. Determine the p.p.m. of potassium in the samples by comparing the meter deflections with standards prepared from KNO_3 and containing from 5 to 80 p.p.m. of potassium in increments of 5 p.p.m.

With the 1.5058-gram sample weight and the designated aliquots and dilutions, the percent potash (K_2O) is computed as the product of the p.p.m. of K as determined from the standard curve and the following factors.

Explanation of Factor:

Gravimetric factor for conversion of K to K_2O.

$$\frac{K_2O}{2K} = 1.2046$$

A. Mg. of K_2O/liter of A. S.* $= \frac{K_2O}{2K}$ x p.p.m. of K

or,

Mg. of K_2O/liter of A. S. = 1.2046 x p.p.m. of K

B. Sample size in mg./liter in A. S. =

$$\frac{\text{mg. of sample}}{\text{volume of boiling flask}} \times \frac{\text{aliquot}}{\text{volume of dilution flask}} \times 1000$$

C. $\%K_2O = \frac{A}{B} \times 100$

Example Calculation:

A 1.5058-gram sample is weighed into a 250 ml. boiling flask, and made to volume; of this, a 25 ml. aliquot is taken and diluted to 250 ml. in the dilution flask.

Size of sample in mg./liter of A. S. =

$$\frac{1505.8}{250} \times \frac{25}{250} \times 1000 = 602.32 \text{ mg.}$$

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*Aspirating solution

$$\%K_2O = \frac{1.2046 \text{ x p.p.m. of K}}{602.32} \text{ x } 100$$

$$\%K_2O = 0.2000 \text{ x p.p.m. of K}$$

Factors:

Aliquot—diluted to—Volume (ml.)		Factor
25	250	0.2000
25	500	0.4000
20	500	0.5000
20	1000	1.0000

Preparation of Standards:

Standard solutions of reagent grade potassium nitrate, containing from 5 to 80 p.p.m. of potassium in increments of 5 p.p.m. were prepared by weighing the calculated amount of dried salt (1.03435 grams diluted to 4 liters), thus giving a stock solution containing 100 p.p.m. of potassium. The standards of low concentration were made up in 500 ml. volumetric flasks. An aliquot of 50 ml. (5 mg. of K) of the stock solution diluted to 500 ml. gives a standard containing 10 p.p.m. of potassium, and each subsequent increase of 25 ml. to the preceding aliquot increases the concentration of the standard by 5 p.p.m. of K.

Preparation of Standard Curve:

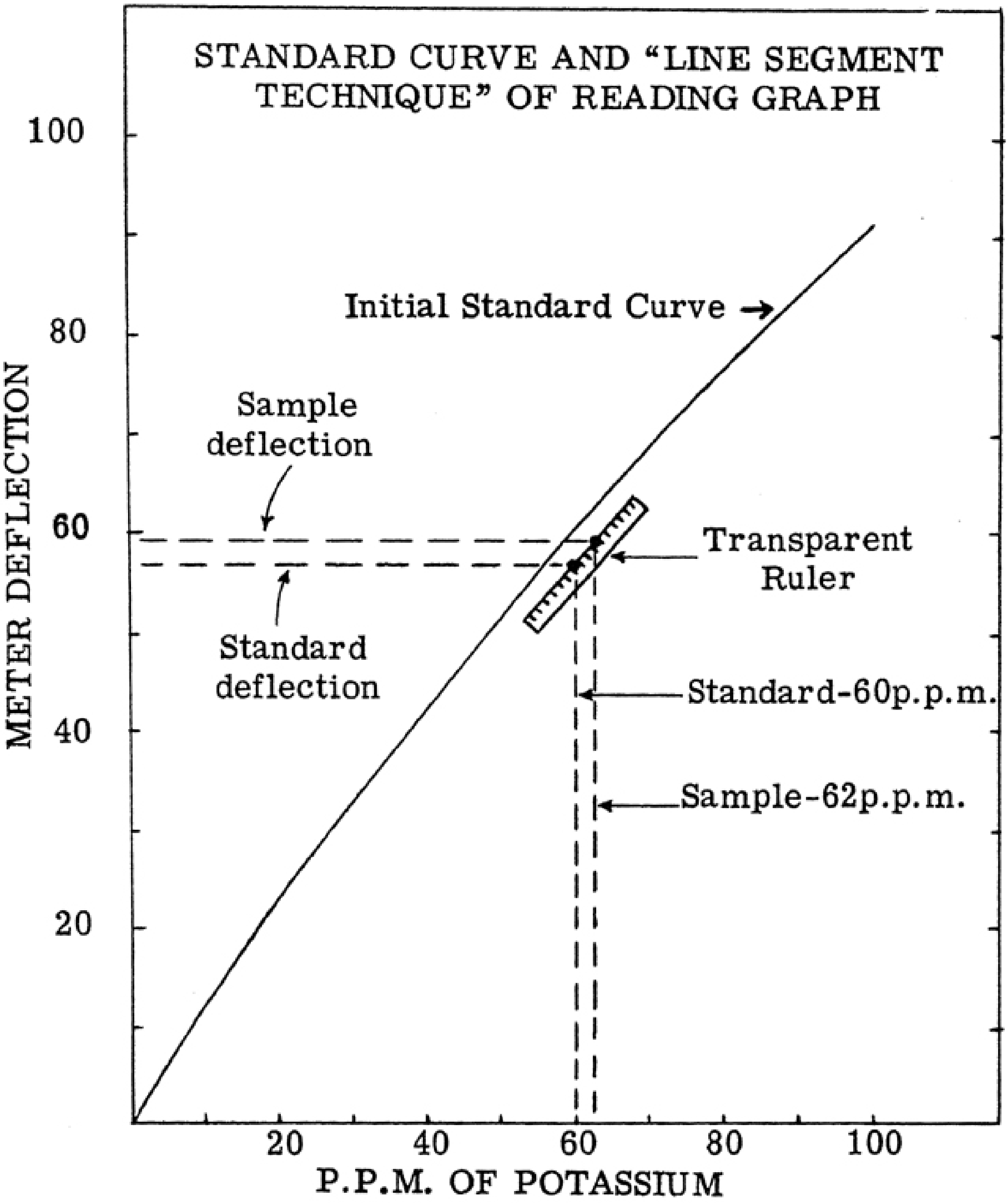
The standard curve of meter deflection at a wave length of 768 mμ versus concentration is made in the conventional manner, using the standard solutions of potassium nitrate of 5 to 80 p.p.m. of potassium in increments of 5 p.p.m. It is essential that the instrument is operating properly with an efficient atomizer in order to avoid readjustments to the instrument and fuel pressure while the initial complete curve is being made,

Plot the above initial curve on the graph allowing 1 inch on the graph to equal 1 p.p.m. of K on the abscissa, and 1 inch on the graph to equal 1 unit of meter deflection on the ordinate.

Reading of Instrument and Graph:

Take the average of three independent meter deflections of the standard with a deflection nearest to the unknown solution and which was read at the same time as the unknown, and plot this point on the graph. If the average obtained from these three independent readings does not fall on the initial curve, lay a ruler parallel to the curve and with the leading edge of the ruler on the new plotted point. This new, short, un-

FIGURE 4



drawn line is the "line segment". It is only essential that this "line segment" be parallel to the initially drawn standard curve between the two points that are being read.

Take the average of three independent meter readings of the unknown sample, and at the point where this reading strikes the leading edge of the ruler, drop down and read the p.p.m. of K on the abscissa for the sample (Figure 4).

In taking the readings of the unknown sample on the instrument it is recommended that FIRST the unknown sample be read and the meter deflection noted. The standard with a meter deflection nearest to the unknown sample is read NEXT. Then alternate until three readings have been obtained on the unknown sample and three on the standard. By this scheme, a reading for the standard is obtained at the same time as the unknown sample. It is assumed that the slope of the curve will not change with various minor instrument changes, i.e., drop in fuel pressure, atomizer performance, etc. With the above method of reading the graph, it is not necessary to keep the instrument readings of the standards on the initially plotted curve. However, it is desirable to maintain the readings for the standards within one deflection unit (1.0) of the initial readings used in preparing the curve.

Instrument and Method Test:

Several potassium salts may be used in a method performance test. Bureau of Standard potassium acid phthalate ($KHC_8H_4O_4$) which theoretically analyzes 23.06% K_2O is one of the more ideal reagents. The following test is suggested for the evaluation of instrument performance, correctness of analytical technique, and accuracy of the prepared standard solutions:

Weigh a sample weight (1.5058 grams) of potassium acid phthalate into a 250-ml. boiling flask and add 500 to 1000 mg. of diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) as an interfering phosphate ion. Using the recommended procedure, analyze the sample for K_2O. The results obtained on this sample from repeated analyses should be within ± 0.1% of the theoretical value (e.g. 23.06 ± 0.1%).

ALTERNATE ION EXCHANGE COLUMN METHOD

Use of ion exchange resin columns in analytical chemistry is time consuming. Considerable time is usually spent in washing sample aliquots through the columns. However, the efficiency and completeness of exchange of ions by column techniques make them superior to the conventional batch methods. For the routine analysis of fertilizers by flame photometry for potassium; a rapid, simple, and effective method was needed to remove the extraneous anions from the sample aliquots. An ion exchange column method which has proven successful and has been in daily use in the Missouri Agricultural Experiment Station chemical laboratories is described below. This method is based on the use of "self feeder" flasks to furnish the wash water automatically, and thus release the chemist for other duties. The laboratory assembly of "self feeder" flask, ion exchange column, and receiving volumetric flask is depicted in Figure 5A. Twelve ion exchange columns (Figure 5) are individually clamped approximately 4 to 5 inches apart in a rack. A notched wooden rack is installed above the columns to hold the inverted "self feeder" flasks containing the wash water (Figure 5A). A removable stainless steel perforated plate is placed in each column. It forms an air cushion between the resin and plate; top and side views of the plate are shown in Figure 5A. Tygon tubing is attached to the stopcocks of the columns, then passed through two-hole rubber stoppers into the receiving volumetric flasks.

Column Procedure:

1. Eliminate steps 6 through 14, (except 12), from the analytical method.
2. Lower the water level in the columns to the level of the resin (1½ inches below the perforated stainless steel plate).
3. Place the stopper and attached tygon tubing in the receiving volumetric flasks.
4. Add a small amount of distilled water (about 5 ml.) on top of the perforated plates. The distilled water should be added rapidly so as to form an air cushion between the resin and the plate. Water can be added to a bank of 12 columns in a few seconds.
5. Add the aliquots of the samples to the distilled water on top of the plates (step 6, page 9).
6. Add two drops of methyl-red indicator and adjust to a pH of 5 with 1:5 nitric acid. Use small 6″ stirring rods to agitate the solutions while adjusting the pH.
7. Open the stopcocks and allow the adjusted aliquots to drip through at a flow rate of 3 to 4 ml. per minute. After the aliquots have lowered to the resin level, close the stopcocks, rinse the stirring rods and perforated plates with a small stream of distilled water (1-3 ml.) and remove the stirring rods.
8. Allow the rinse water to lower to the resin level.
9. Invert the distilled water "self feeder" flasks into the top of the columns. Do this quickly to maintain an air cushion between the plates and the resin.
10. Open the stopcocks and allow to drip at 4 to 6 ml. per minute until a minimum of 100 ml. has been collected.
11. Open the stopcocks completely until the "self feeder" flasks are empty. Do not permit the water level in the columns to fall below the resin level.
12. Remove the receiving flasks, mix thoroughly, and make to volume.

FIGURE 5

ION EXCHANGE COLUMN

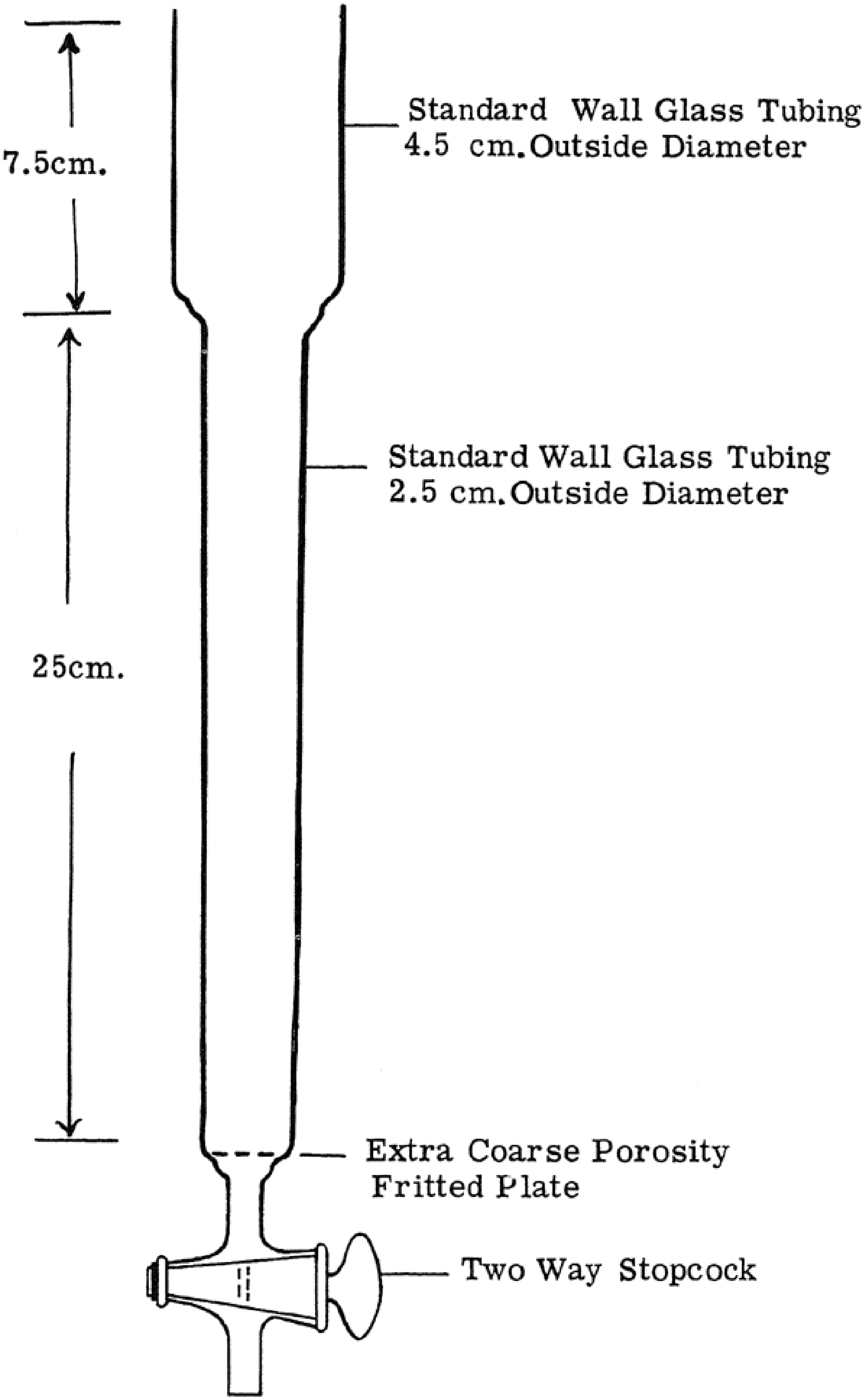
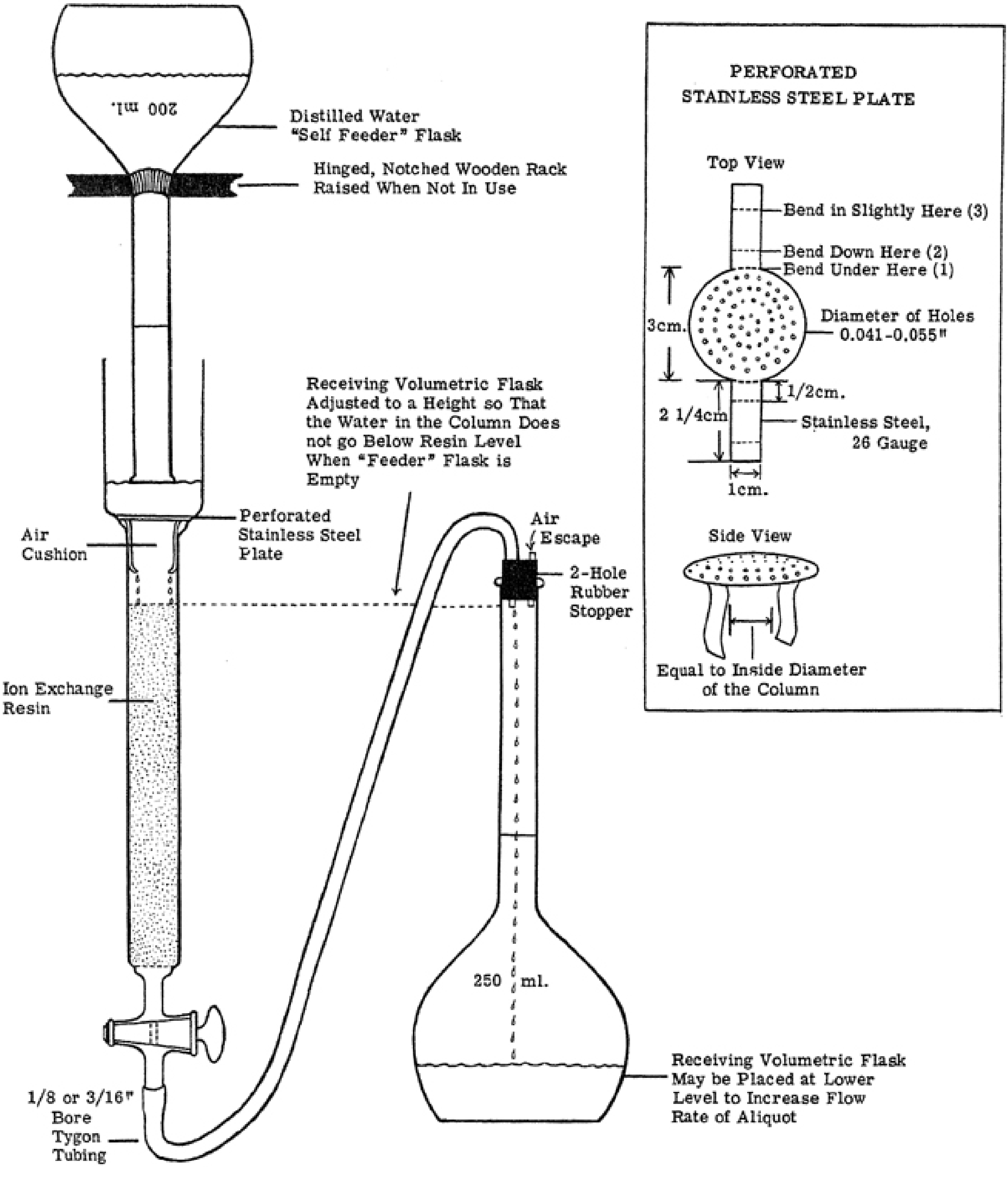


FIGURE 5A

LABORATORY ASSEMBLY OF ION EXCHANGE COLUMN, SELF FEEDER, & RECEIVING FLASKS



In this procedure the receiving flasks may be placed directly under the ion exchange columns; however, in doing this, care must be exercised to prevent the water level in the columns from going below the resin level when the "feeder flasks" become empty. If the water is allowed to drain from the resin, air will become trapped in the resin column and the subsequent aliquots and wash water will "channel" through the resin with incomplete ion removal and washing. By using the flexible tygon tubing, the inlet to the receiving flasks may be adjusted to a height equal to the top of the resin. The flow-rate of the aliquot can be increased by placing the receiving flasks at a lower level before the additional "head" is obtained with the added wash water.

The volume of the "self feeder" flask should be such that its volume, when added to the volume of the aliquot, rinse water, and 1:5 nitric acid used in pH adjustment, will not exceed the volume of the receiving flask.

The stainless steel perforated plate serves the purpose of separating the two liquid systems and providing an air cushion between them. With the described column and perforated plate a transfer step is eliminated. When air bubbles pass up into the neck of the "feeder flasks," any liquid in contact with the mouth of the feeder flask also will be carried partially into the flask. It is essential to have only distilled water above the perforated plate, and thus avoid incomplete transfer of the sample aliquot.

PART II

ION EXCHANGE COLUMN AND BATCH STUDIES

In preliminary investigations with Amberlite IR-4B-NO_3 both the ion exchange column and batch methods were effective in removing phosphates from a sample solution, and the potassium added to the samples was quantitatively recovered (Tables 1 and 2).

TABLE 1. RESIN EXHAUSTION STUDY AND COMPLETENESS OF REMOVAL OF PHOSPHATE BY AN ION EXCHANGE COLUMN OF IR-4B-NO_3

Aliquot No.	K_2O Found, % Resin Column A	 Resin Column B
1	8.14	7.98
2	7.90	8.02
3	8.00	8.05
4	8.07	8.00
5	7.98	7.98
6	7.98	8.02
7	8.02	8.05
8	8.10	7.95
9	7.93	8.02
10	8.02	8.00
Avg.	8.01	8.01

Ten consecutive 25-ml. aliquots were passed through each column. Each aliquot passed through Column A contained 10 mg. of K as KNO_3. Each aliquot passed through Column B contained 10 mg. of K as KNO_3 + 36.1 mg. of P_2O_5 as $(NH_4)_2HPO_4$.

Theoretical value of each sample when diluted to 250 ml. total volume was 8.00% K_2O.

TABLE 2. RESIN CONTACT TIME STUDIES ON REMOVAL OF PHOSPHATE WITH AMBERLITE IR-4B-NO_3; BATCH METHOD.

Sample No.	Resin-sample Contact Time Minutes	Magnetic Stirring Mg. of P_2O_5*	Mixed for 5 Seconds at 5 Minute Intervals in resin contacted samples	Mixed 1 Minute, Allowed to Stand 4 Hours, then Mixed 1 Minute
1	1	2.00		
2	2	1.25		
3	3	1.35		
4	5	1.45	1.25	
5	10	1.45	1.55	
6	30	1.00	1.00	
7	60	1.00	1.00	
8	240			1.25

Each sample aliquot initially contained 36.1 mg. of P_2O_5 prior to contact with 30 ml. of damp IR-4B-NO_3 resin.

*Each value is an average of two independent determinations.

Column Method of Anion Removal:

Ten consecutive 25-ml. aliquots were passed through two ion exchange columns, A and B, which were 6 inches long and contained about 70 ml. of IR-4B-NO_3 resin. The flow rate of the aliquot and wash water was 6 to 8 ml. per minute. Each aliquot passed through Column A contained 10 mg. of K as KNO_3. Each aliquot passed through Column B contained 10 mg. of K as KNO_3 and 36.1 mg. of P_2O_5. The amount of potassium in each aliquot was equivalent to the amount present in the sample aliquot of an 8.00% K_2O fertilizer. Thus, each initial sample aliquot when made to a final total volume of 250 ml. theoretically contained 40 p.p.m. of K and 144.4 p.p.m. of P_2O_5.

The flame results on the effluent solutions from Column A (Table 1) indicated that there was no retention of the potassium by the resin. The flame results on the effluent solutions from Column B indicated that the phosphate ion was removed from all aliquots to a level whereby the emission intensity of the potassium was not depressed. In the interference studies it was shown conclusively that the emission intensity of K was decreased if the concentration of P_2O_5 were over 5.5 p.p.m. in the aspirating solution.

Batch Method of Anion Removal:

A resin "contact time" study by the batch method was conducted with the resin IR-4B-NO_3. The resin-aliquot contact time varied from 1 minute to 4 hours, and the types of agitation were continuous or intermittent. Thirty ml. of damp IR-4B-NO_3 resin were used and each sample aliquot initially contained 36.1 mg. of P_2O_5. A rapid removal of phosphate ions occurred with either intermittent or continuous agitation, and at least 96% of the added P_2O_5 was removed within a period of 5 minutes (Table 2). Amberlite IR-4B was very effective in removing anions and this batch method is recommended for routine work. Later, it was shown in both batch and column removal studies on 12 commercial ion exchange resins containing different functional groups that Amberlite IR-4B was ideally suited for this method because of its high affinity for the phosphate ion (Tables 31, 32, and 33). The ion exchange resins, Amberlite IR-45, IRA-400, Dowex 3, Dowex 1, Duolite A-6, A-40, A-70, A-41, A-7, Permutit-S, and DeAcidite, were found not adaptable for the removal of anions from sample aliquots by the batch method. The following resins were found satisfactory when using the column technique: Amberlite IR-4B, Duolite A-7, DeAcidite, Duolite A-41 Permutit-S, and Dowex 1.

PART III

ANION AND CATION INTERFERENCE STUDIES

The accurate analysis of biological fluids, inorganic materials, and many other substances for K^+, Na^+, Ca^{++}, and Mg^{++} by flame photometric methods requires that the presence of extraneous anions and cations be considered. Various cations and anions, e.g. sodium, calcium, magnesium, sulfate, phosphate, and oxalate, are known to either enhance or depress the flame emission intensity of metals such as potassium, sodium, and calcium. Sulfate (4), phosphate (4), and aluminate (20), when present in concentrations of the same order of magnitude as those of the alkaline earths, cause a considerable and striking reduction of the emission intensity of magnesium, calcium, and strontium. A number of other workers have reported on the mutual interference of sodium, calcium, magnesium, and potassium (5, 12, 13, 23, 25).

Alkemade (1), in a report on the effect of sodium on potassium radiation, explained the increase of potassium emission intensity as due mainly to repression of potassium ionization by electrons produced by the ionized sodium; thus the atomic emission intensity of potassium was increased. He also reported on factors and forms of spray interference, such as temperature of solution, organic components, salts, rate of liquid intake, evaporation, supply of spray and vapor to the flame, and flame temperature.

The suppression of the flame emission intensity of metals by anions apparently is due, in part, to the formation of chemical compounds of high melting and boiling points which have a lowered emission intensity (17). Background, of course, is another major contributing cause of interference and is due to other radiating species in the aspirating solution. It has been reported (17) that extraneous cations produce heterochromatic background radiation and have no effect on the monochromatic emission intensity measured above background.

Several methods are used in correcting for various types of interferences in flame analysis, such as dilution, addition of radiation buffers, use of internal standards, the addition of standards at different levels to the sample, and the correction of desired line intensity for background. These methods have contributed significantly to the control of interfering effects.

During the past three years experiments have been conducted in the Missouri laboratories on the application of cation and anion ion exchange resins and chemical pretreatment to clean up the sample solutions of extraneous ions prior to aspiration into the flame. In this way the sample aspirating solution becomes a simple system and is compared to a standard containing only potassium nitrate. The results obtained in these experiments on synthetic samples and fertilizer samples are presented in the following tables and graphs.

The effect of extraneous cations and anions on the emission intensity of potassium was evaluated as follows: A series of standards of known p.p.m. of K were prepared. Different concentrations of the ions under investigation were added to these standards. All of the standards of known concentration were usually made from aliquots of a common stock solution of 100 p.p.m. of K (1.0343 g. of reagent grade KNO_3 diluted to 4 liters). One standard of each series contained only potassium nitrate. The meter deflection of this standard was used as the reference point of "no effect." The cations investigated were added as nitrates, and all the anions were added as the ammonium salts. Results obtained in preliminary phases of this investigation indicated that ammonium and nitrate ions had no effect on the meter deflection of potassium.

In most cases, three different standards were used in each study. These contained 20, 25, and 30 p.p.m. of potassium, respectively. The different cations and anions were added at various levels, usually extending over the concentration range of 5 to 5000 p.p.m. In this way the effect of varying concentrations of extraneous ions on three different potassium standards were determined.

To compensate for instrument drift, change in fuel pressure, atomizer performance, etc., the readings were first taken from low to high concentration of interfering ion with a particular standard. Then readings were taken from high to low; lastly, the readings were taken alternately first on a standard with a low concentration of interfering ion, then high, low, etc., until all the readings were completed.

Results of the interference studies are in Tables 3 to 13, and Figures 6 to 11. The effects of pH and temperature of the aspirating solution on the meter deflection of potassium standards are given in Tables 14 and 15, and Figures 12 and 13.

RESULTS OF ANION AND CATION INTERFERENCE STUDIES

The interference effects of the various cations, anions, temperature, pH, formaldehyde, and urea on the emission intensity of potassium are shown in the following tables. These tables show the enhancement or suppression of the meter deflection values. This of course will vary, and is meant to be interpreted as a trend, and not that these identical results will be obtained by other investigators. Such factors as the make and type of the instrument, initial adjustment of the instrument, fuel and oxygen pressure, efficiency of atomization, flame temperature, and linearity of the curve are all conditions contributing to the readings obtained. The Beckman DU spectrophotometer with flame attachment used in this investigation was adjusted to give a spread of approximately 5-meter deflection units for standards of 20 to 25 p.p.m., and about 3-meter deflection units for each 5 p.p.m. increment of standard as the curve leveled off for the higher standards, e.g. 75 p.p.m. Thus, in this investigation, each change of one unit in the meter deflection value represents 1 to 2 p.p.m. of potassium in the aspirating solution. With the recommended dilution for a commercial fertilizer containing less than 12% K_2O, an observed change of 1 p.p.m. of potassium in the aspirating solution will change the K_2O content by 0.2%.

Phosphate at a level of about 5 p.p.m. depressed the emission intensity of potassium slightly, about 0.1 of a meter deflection unit. This effect became more pronounced as the concentration of phosphate increased, and at a level of 500 p.p.m. the meter deflection values were lowered by about 2 units for potassium standards of 20, 30, and 40 p.p.m. (Refer to Table 3 and Figure 6). The same observation on phosphate interference was evident in the low recovery values for potassium for the "unprocessed" set of synthetic samples (Table 18), as compared to the "processed" set in which the phosphates were removed with ion exchange resins.

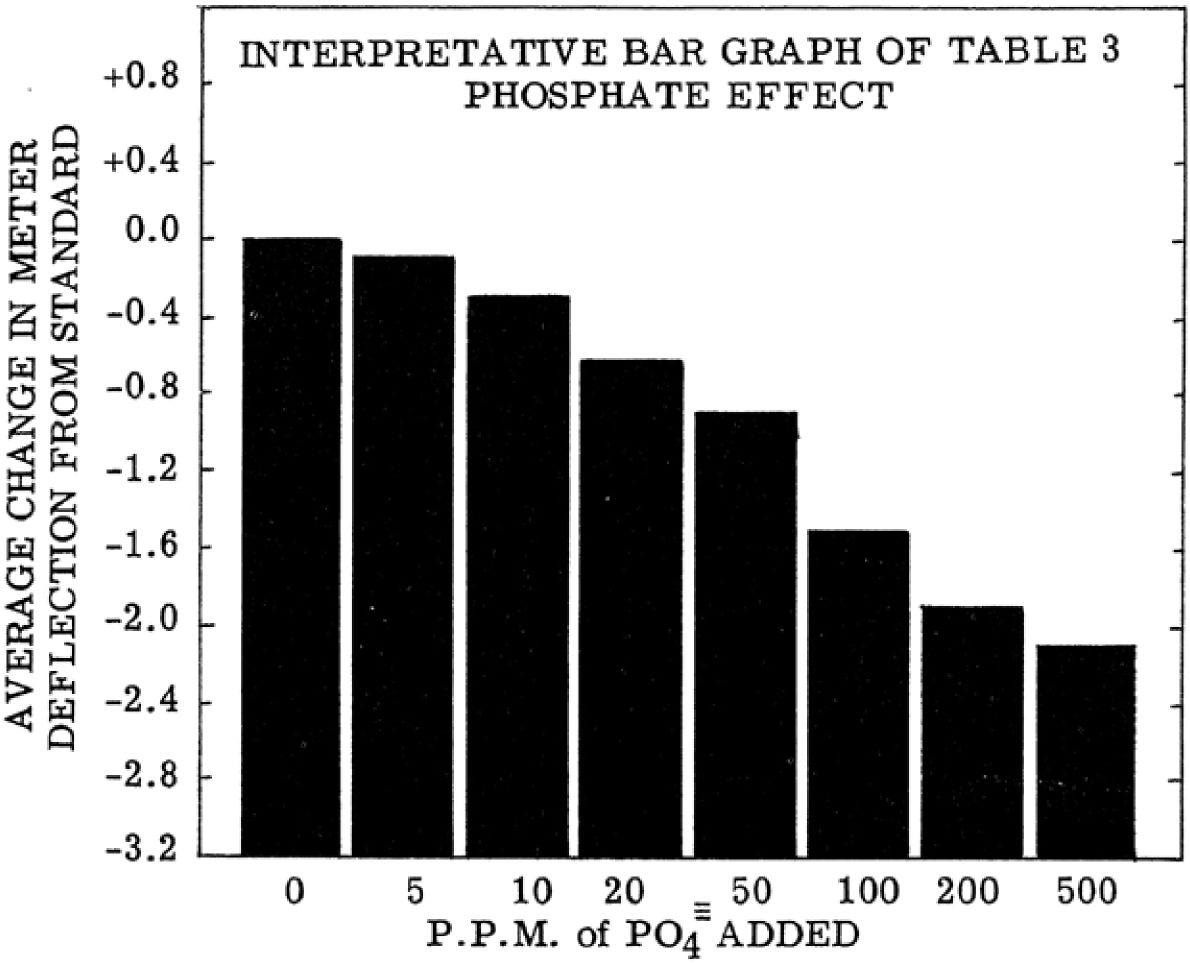
TABLE 3. EFFECT OF PHOSPHATE ON THE METER DEFLECTION OF POTASSIUM

Conc.* of $PO_4^{\equiv}$	Potassium Standards, P.P.M.		
	20	30	40
P.P.M.	Meter Deflection**		
0	20.0	25.0	30.0
5	19.9	24.9	29.9
10	19.8	24.5	29.7
20	19.6	24.2	29.4
50	19.1	23.7	28.9
100	18.8	23.4	28.2
200	18.1	23.0	28.1
500	18.1	22.6	28.0

*Phosphate added as $(NH_4)_2HPO_4$ from a stock solution of 2500 p.p.m. of $PO_4^{\equiv}$.

**Each meter deflection value is an average of 3 independent observations.

FIGURE 6



Each bar graph shows the average depressant effect of phosphate on all standards of potassium investigated.

For example (Table 3), 5 p.p.m. of Phosphate depressed the meter defection 0.1 unit for each standard of 20, 30, & 40 p.p.m. of potassium. The average effect was 0.1 unit.

The emission intensity of potassium was enhanced by oxalate, added as ammonium oxalate, at concentrations up to 1000 p.p.m. The peak enhancement occurred at approximately 800 p.p.m. of oxalate (Table 4 and Figure 7). At the 4000 p.p.m. level and above the meter deflection values for potassium were depressed. Also, the data in Table 19 indicate slightly higher recovery values for potassium in the "unprocessed" synthetic samples.

TABLE 4. EFFECT OF OXALATE ON THE METER DEFLECTION OF POTASSIUM

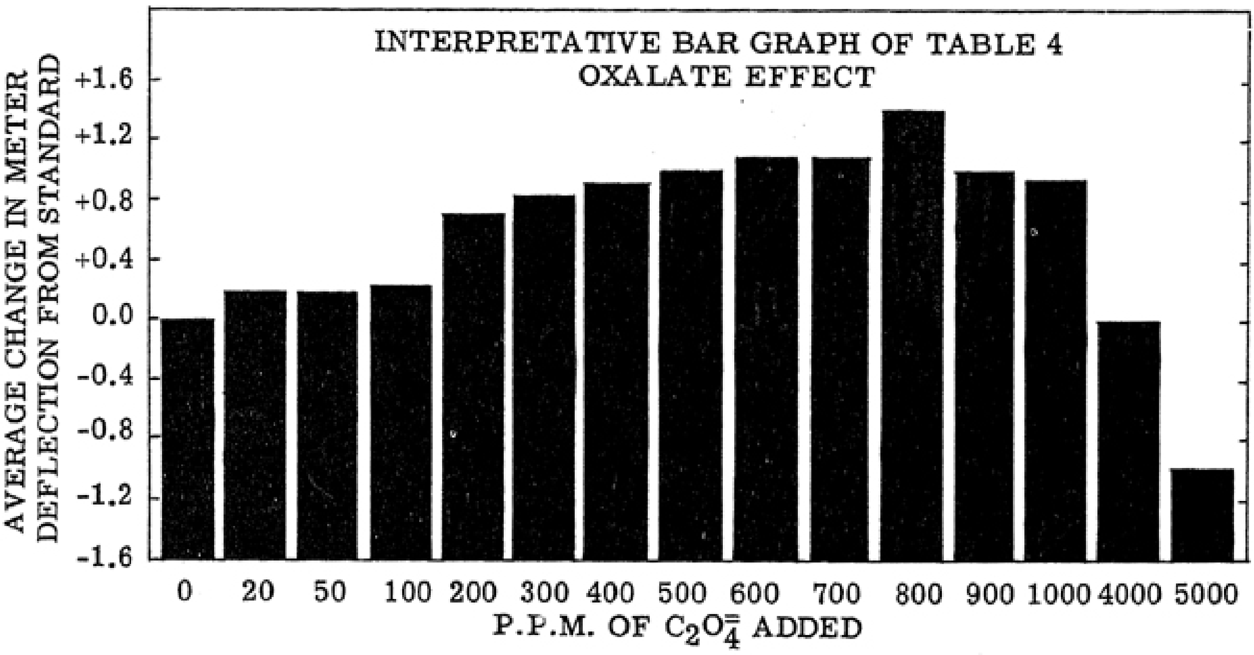
Conc. of $C_2O_4^{=}$*	Potassium Standards, P.P.M.		
	20	30	40
P.P.M.	Meter Deflection**		
0	20.0	25.0	30.0
20	20.1	25.2	30.2
50	20.1	25.2	30.3
100	20.2	25.2	30.3
200	20.5	25.8	30.7
300	20.6	26.0	30.8
400	20.7	26.1	30.8
500	20.7	26.1	30.9
600	20.8	26.2	31.1
700	20.8	26.2	31.1
800	21.3	26.7	31.6
900	20.9	26.1	31.0
1000	20.5	26.1	30.9
4000***	19.9	25.1	29.9
5000***	19.2	23.5	29.3

*Oxalate added as $(NH_4)_2C_2O_4 \cdot H_2O$ from a stock solution of 5,000 p.p.m. of $C_2O_4^{=}$.

**Each meter deflection value is an average of 3 independent observations.

***Added as Solid.

FIGURE 7



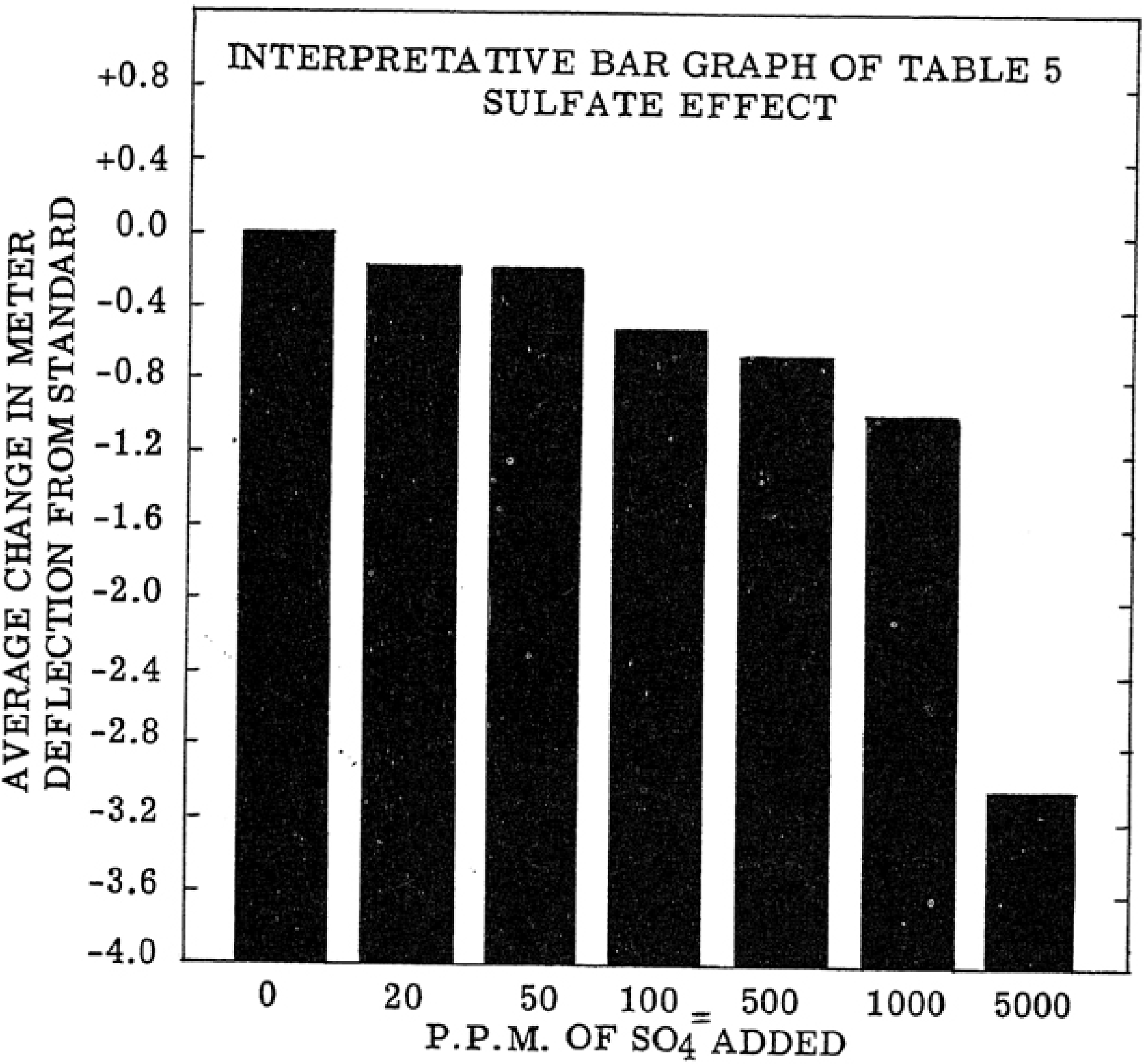
Each bar graph shows the effect of oxalate on all standards of potassium investigated.

Explanation same as for Figure 6.

Data are presented in Table 5 and Figure 8 on the effect of sulfate on potassium emission. The results show a striking parallel to those for phosphate. A marked depression of the potassium emission was noted in samples containing sulfate at concentrations of 100 p.p.m. and greater, and some depressant effect was observed in samples containing from 20 to 50 p.p.m. of sulfate. At a level of 5000 p.p.m. the meter deflection was depressed by 3 units. Also, the recovery data in Table 20 definitely show that low results were obtained for the "unprocessed" synthetic samples.

From all indications the ammonium and chloride ions individually have no effect on the emission intensity of potassium. Ammonium nitrate added at levels up to 2000 p.p.m. of NO_3^- to KNO_3 and KCl standards

FIGURE 8



Each bar graph shows the effect of sulfate on all standards of potassium investigated.

Explanation same as for Figure 6

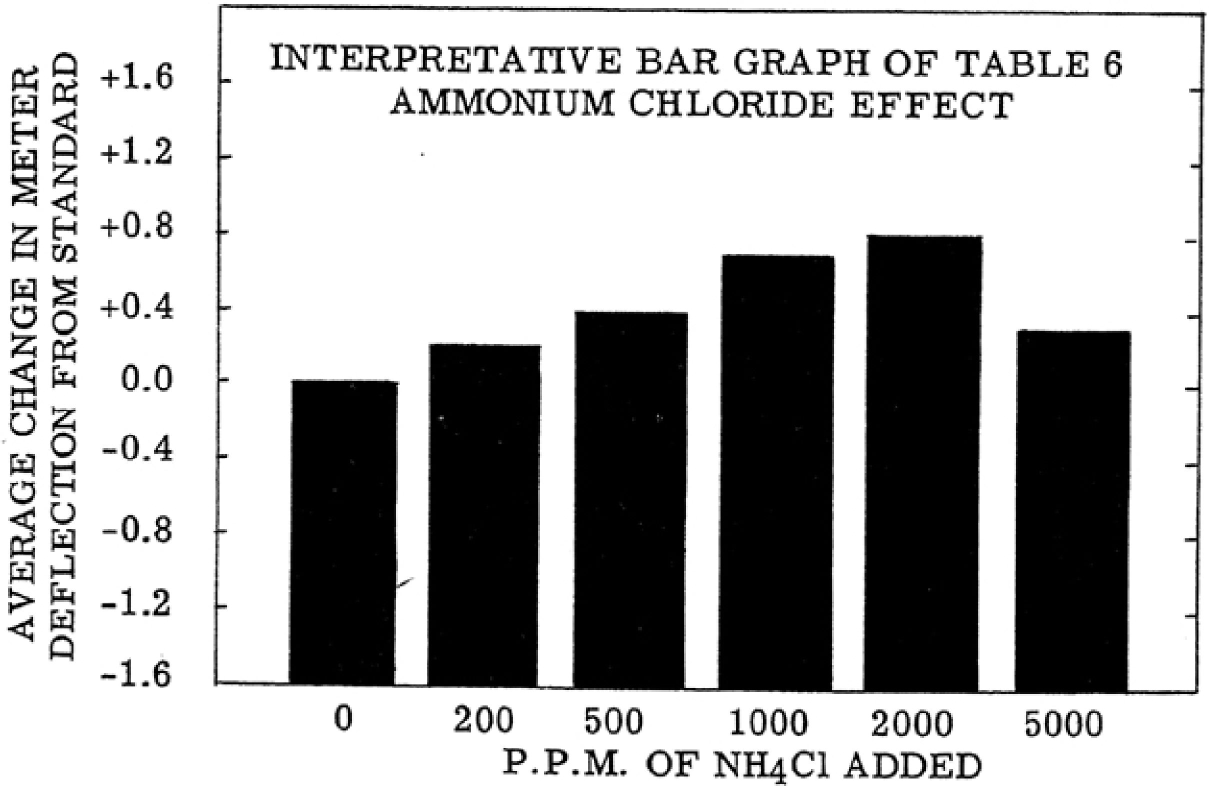
TABLE 5. EFFECT OF SULFATE ON THE METER DEFLECTION OF POTASSIUM

Conc. of $SO_4^{=}$*	Potassium Standards, P.P.M.		
	20	30	40
P.P.M.	Meter Deflection**		
0	20.0	25.0	30.0
20	19.6	24.9	29.9
50	19.6	24.9	29.8
100	19.5	24.3	29.8
500	19.4	24.1	29.3
1000	19.1	23.8	29.0
5000***	17.9	22.1	26.0

*Sulfate added as $(NH_4)_2SO_4$ from a stock solution of 2,500 p.p.m. of $SO_4^{=}$.
**Each meter deflection value is an average of 3 independent observations.
***Added as solid.

(Table 8) showed no significant effect. The concentration of ammonium nitrate in the aspirating solution of fertilizer samples usually does not exceed this amount. The emission intensity values were the same for standards of equal p.p.m. of K prepared from KCl or KNO_3. However, the addition of 200 to 2000 p.p.m. of NH_4Cl to KNO_3 and KCl standards produced a marked increase in the meter deflection (Table 6, Figures 1 and 9). This increase reached a maximum at about 2000 p.p.m. of NH_4Cl, remained on a plateau through 4000 p.p.m., and then dropped off at 5000.

FIGURE 9



Each bar graph shows the effect of ammonium chloride on all standards of potassium investigated. Explanation same as for Figure 6.

TABLE 6. EFFECT OF AMMONIUM CHLORIDE ON THE METER DEFLECTION OF POTASSIUM

Conc. of NH_4Cl*	Potassium Standards, P.P.M. 20	30	40
P.P.M.	Meter Deflection**		
0	20.0	25.0	30.0
200	20.1	25.3	30.2
500	20.3	25.6	30.4
1000	20.5	25.6	31.0
2000	20.5	25.9	31.0
5000***	20.2	25.4	30.2

*Ammonium chloride added from a stock solution of 2,500 p.p.m. of NH_4Cl.

**Each meter deflection value is an average of 3 independent observations.

***Added as solid.

The decrease at 5000 p.p.m. probably is due to a change in the physical properties of the aspirating solution.

The presence of carbonate as ammonium carbonate at concentrations greater than 100 p.p.m. definitely enhanced the emission intensity of potassium (Table 7). However, carbonates are removed as CO_2 from the sample aliquot on adjustment of the pH to 5 with dilute HNO_3 and this interference is thus removed.

TABLE 7. EFFECT OF CARBONATE ON THE METER DEFLECTION OF POTASSIUM

Conc. of $CO_3^{=}$*	Potassium Standards, P.P.M. 20	30	40
P.P.M.	Meter Deflection**		
0	20.0	25.0	30.0
20	20.0	25.0	30.0
50	20.0	25.0	30.0
100	20.1	25.0	30.0
500	20.8	25.6	31.2
1000	20.9	25.6	31.3
5000***	20.7	25.4	30.9

*Carbonate added as $(NH_4)_2CO_3 \cdot H_2O$ from a stock solution of 2,500 p.p.m. of $CO_3^{=}$.

**Each meter deflection value is an average of 3 independent observations.

***Added as solid.

TABLE 8. EFFECT OF NITRATE ON THE METER DEFLECTION OF POTASSIUM

Conc. of NO_3^-*	Potassium Standards, P.P.M. 20	30	40	50	60	70
P.P.M.	Meter Deflection**					
0	20.0	25.0	30.0	35.0	40.0	45.0
100	20.0	25.0	30.0	35.0	39.9	44.8
500	20.0	24.9	30.1	35.0	40.0	44.7
1000	20.0	25.0	30.1	35.0	40.0	44.8
2000	20.0	25.0	30.0	35.2	40.0	44.9

*Nitrate added as NH_4NO_3 from a stock solution of 2,500 p.p.m. of NO_3^-.

**Each meter deflection value is an average of 3 independent observations.

Magnesium added as magnesium nitrate at a level of 1000 p.p.m. to standards produced no effect on the emission intensity of potassium (Table 9). At a concentration of 5000 p.p.m. a slight enhancement was observed. The recovery of potassium from synthetic samples was not affected by the presence of magnesium (Table 22). It was concluded that magnesium could be disregarded in the flame analysis of commercial fertilizers for potassium.

TABLE 9. EFFECT OF MAGNESIUM ON THE METER DEFLECTION OF POTASSIUM

Conc. of Mg^{++}*	Potassium Standards, P.P.M. 20	30	40
P.P.M.	Meter Deflection**		
0	20.0	25.0	30.0
5	20.0	25.0	30.1
10	20.0	24.8	29.9
20	20.0	24.9	29.9
50	20.0	24.9	30.2
100	20.0	24.9	30.1
300	19.9	24.8	29.8
1000	19.9	24.9	29.9
5000***	20.7		31.0

*Magnesium added as $Mg(NO_3)_2 \cdot 6H_2O$ from a stock solution of 2,500 p.p.m. of Mg^{++}.

**Each meter deflection value is an average of 3 independent observations.

***Added as solid.

Data are presented in Table 10 and Figure 10 on the effect of calcium on the emission intensity of potassium. A definite enhancement of the potassium emission occurred at a concentration of calcium of 20 p.p.m. and greater. During the preparation of the fertilizer sample solution, ammonium carbonate or oxalate is added and the calcium content is reduced. It was found that the final aspirating solution contained between 2 and 8 p.p.m. of calcium. This amount of calcium is appreciably below the concentration needed to produce a significant effect (Table 23).

TABLE 10. EFFECT OF CALCIUM ON THE METER DEFLECTION OF POTASSIUM

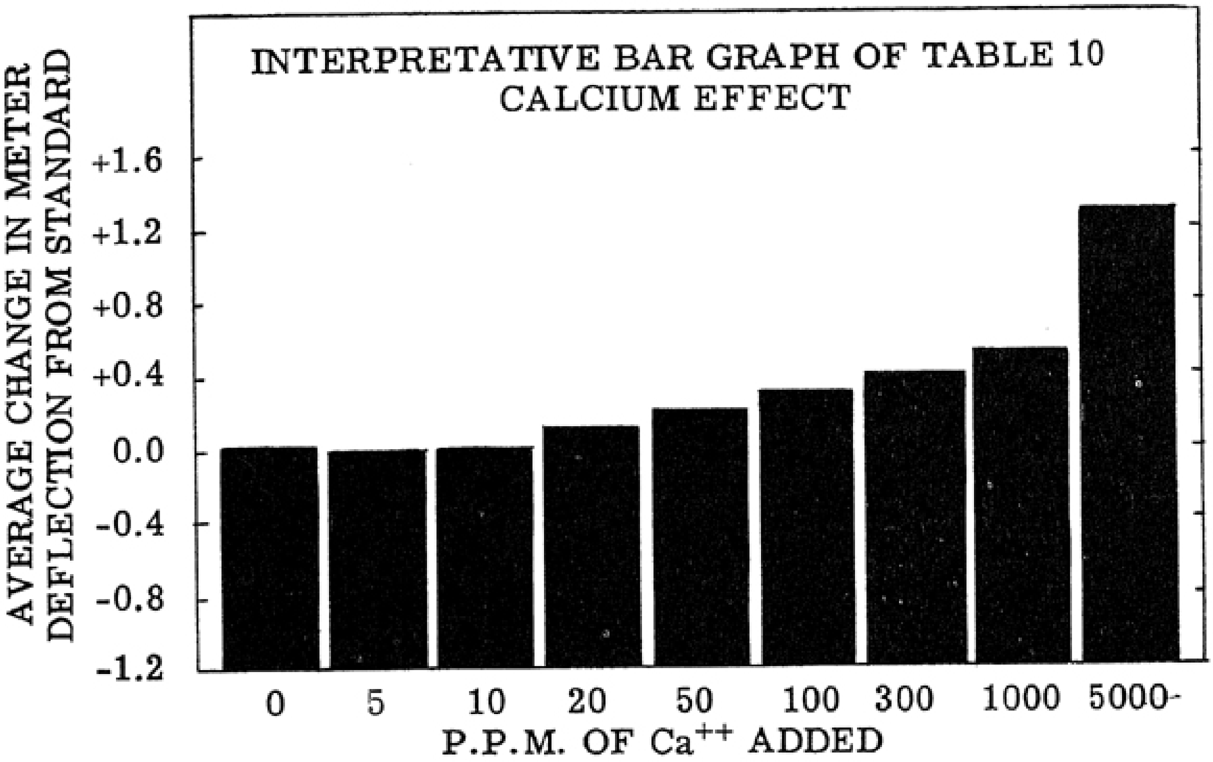
Conc. of Ca^{++}*	Potassium Standards, P.P.M. 20	30	40
P.P.M.	Meter Deflection**		
0	20.0	25.0	30.0
5	20.0	25.0	30.0
10	20.0	25.0	30.0
20	20.1	25.0	30.1
50	20.2	25.2	30.2
100	20.3	25.3	30.2
300	20.4	25.5	30.3
1000	20.6	25.5	30.5
5000***	21.2	26.3	

*Calcium added as $Ca(NO_3)_2 \cdot 4H_2O$ from a stock solution of 2,500 p.p.m. of Ca^{++}.

**Each meter deflection value is an average of 3 independent observations.

***Added as solid

FIGURE 10



INTERPRETATIVE BAR GRAPH OF TABLE 10
CALCIUM EFFECT

Each bar graph shows the effect of Calcium on all standards of potassium investigated.

Explanation same as for Figure 6

TABLE 11. EFFECT OF SODIUM ON THE METER DEFLECTION OF POTASSIUM

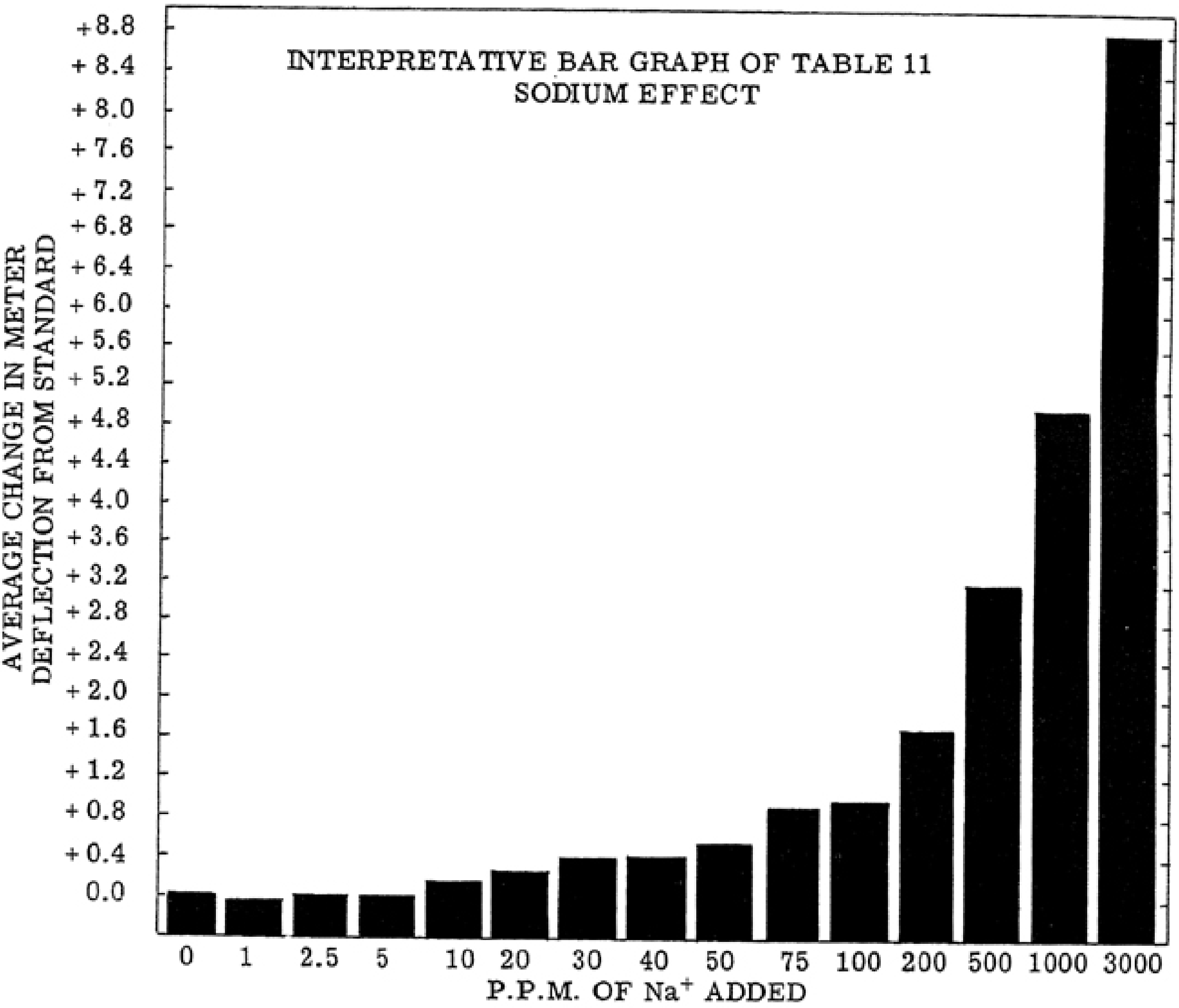
Conc. of Na+* P.P.M.	Potassium Standards, P.P.M. 20	30	40
	Meter Deflection**		
0	20.0	25.0	30.0
1	19.9	25.0	29.9
2.5	20.0	25.0	30.1
5	20.0	25.1	30.0
10	20.1	25.1	30.0
20	20.1	25.3	30.2
30	20.3	25.5	30.3
40	20.3	25.6	30.4
50	20.3	25.5	30.7
75	20.8	25.9	31.1
100	20.9	26.0	31.2
200	21.4	26.5	32.1
500	22.5	28.2	33.9
1000	23.9	30.1	35.9
3000	26.9	34.0	40.4

*Sodium added as $NaNO_3$ from a stock solution of 500 p.p.m. of Na+ for concentrations of 1 to 40 p.p.m. in the aspirating solution, and from a stock solution of 25,000 p.p.m. for concentrations of 50 to 3,000 p.p.m.

**Each meter deflection value is an average of 3 independent observations.

A significant increase in the emission intensity of potassium was obtained when the sodium content of the aspirating solution was 10 p.p.m. or above (Table 11 and Figure 11). As sodium is not removed in the proposed method, a concentration greater than 10 p.p.m. would seriously interfere unless known amounts were added to both the standards and samples. The aliquots and dilutions recommended in the proposed method for commercial fertilizers are such that rarely does the sodium content in the final aspirating solution exceed 1 to 2 p.p.m.

FIGURE 11



Each bar graph shows the effect of Sodium on all standards of potassium investigated.

Explanation same as for Figure 6

Urea at a level of 1000 p.p.m. produced no effect on the emission of potassium (Table 12).

TABLE 12. EFFECT OF UREA ON THE METER DEFLECTION OF POTASSIUM

Conc. of $(NH_2)_2CO$*	Potassium Standards, P.P.M.		
	20	30	40
P.P.M.	Meter Deflection**		
0	20.0	25.0	30.0
5	20.0	25.0	30.1
20	20.0	25.0	30.1
50	20.0	25.0	30.0
100	20.0	24.9	30.0
200	20.0	25.0	30.0
500	20.0	24.9	30.0
1000	20.0	25.0	30.1

*Urea added from a stock solution of 2,500 p.p.m. of urea.

**Each meter deflection value is an average of 3 independent observations.

Formaldehyde was considered as a reagent to tie up the ammonium ions. However, formaldehyde so extremely affected the emission intensity of potassium that further use of it was not tried (Table 13).

TABLE 13. EFFECT OF FORMALDEHYDE ON THE METER DEFLECTION OF 20 P.P.M. OF POTASSIUM

Sample No.	Ml. of 38% CH_2O added*	Meter Deflection**
1	0	20.0
2	5	20.9
3	10	22.0
4	15	22.8
5	20	23.1
6	25	23.2
7	100	27.8

*Total volume of aspirating solution was 500 ml.

**Each meter deflection value is an average of 3 independent observations.

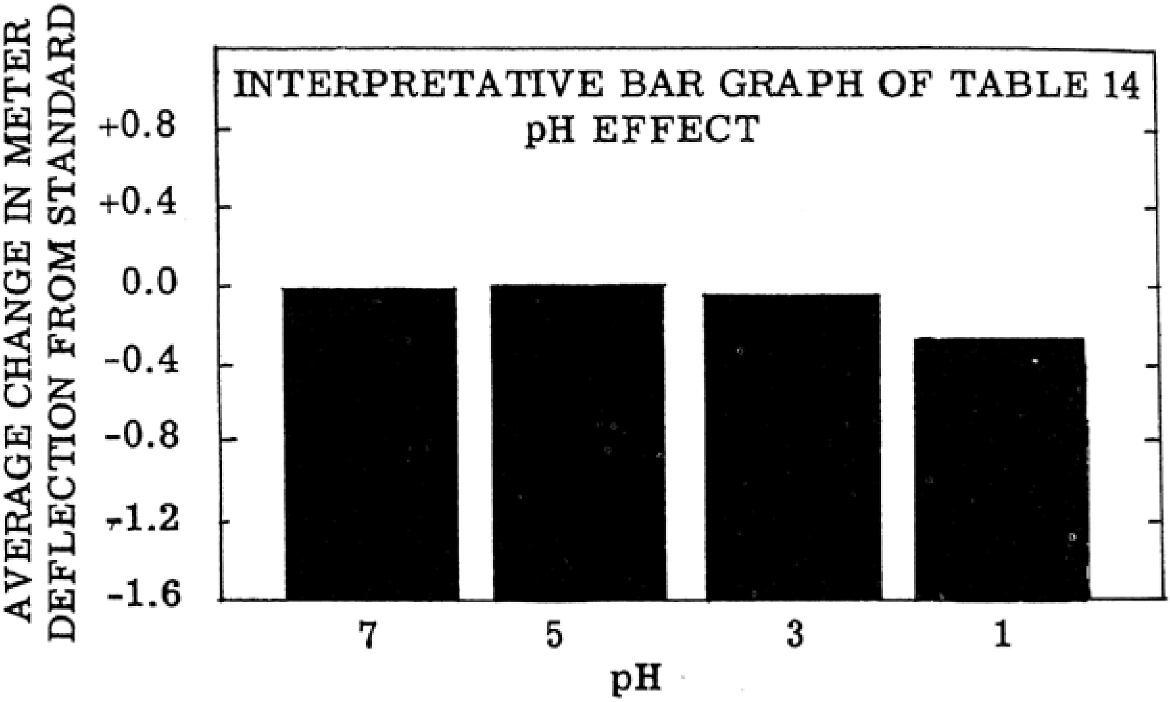
TABLE 14. EFFECT OF pH ON THE METER DEFLECTION OF POTASSIUM

pH of Aspirating Solution	Potassium Standards, P.P.M.		
	20	30	40
	Meter Deflection*		
7	20.0	25.0	30.0
5	20.0	25.0	29.9
3	20.0	24.9	29.9
1	19.8	24.8	29.7

*Each meter deflection value is an average of 3 independent observations.

Potassium standards were adjusted to pH values of 1, 3, 5, and 7 with dilute nitric acid. A slight suppression of the emission intensity of potassium was observed at a pH of 1. The temperature of the aspirating solution of the samples should be within a ± 3° C range of the standards with which they are compared. A very serious error would occur if the

FIGURE 12



Each bar graph shows the effect of pH on all standards of potassium investigated.

Explanation same as for Figure 6

dilutions were made with cold or warm distilled water and the sample solutions were then aspirated. A decrease in temperature of the aspirating solution from 29 to 8° C depressed the meter deflection 5.1 units, and a difference of only 3° C depressed the reading by 0.8 of a unit (Table 15 and Figure 13).

FIGURE 13

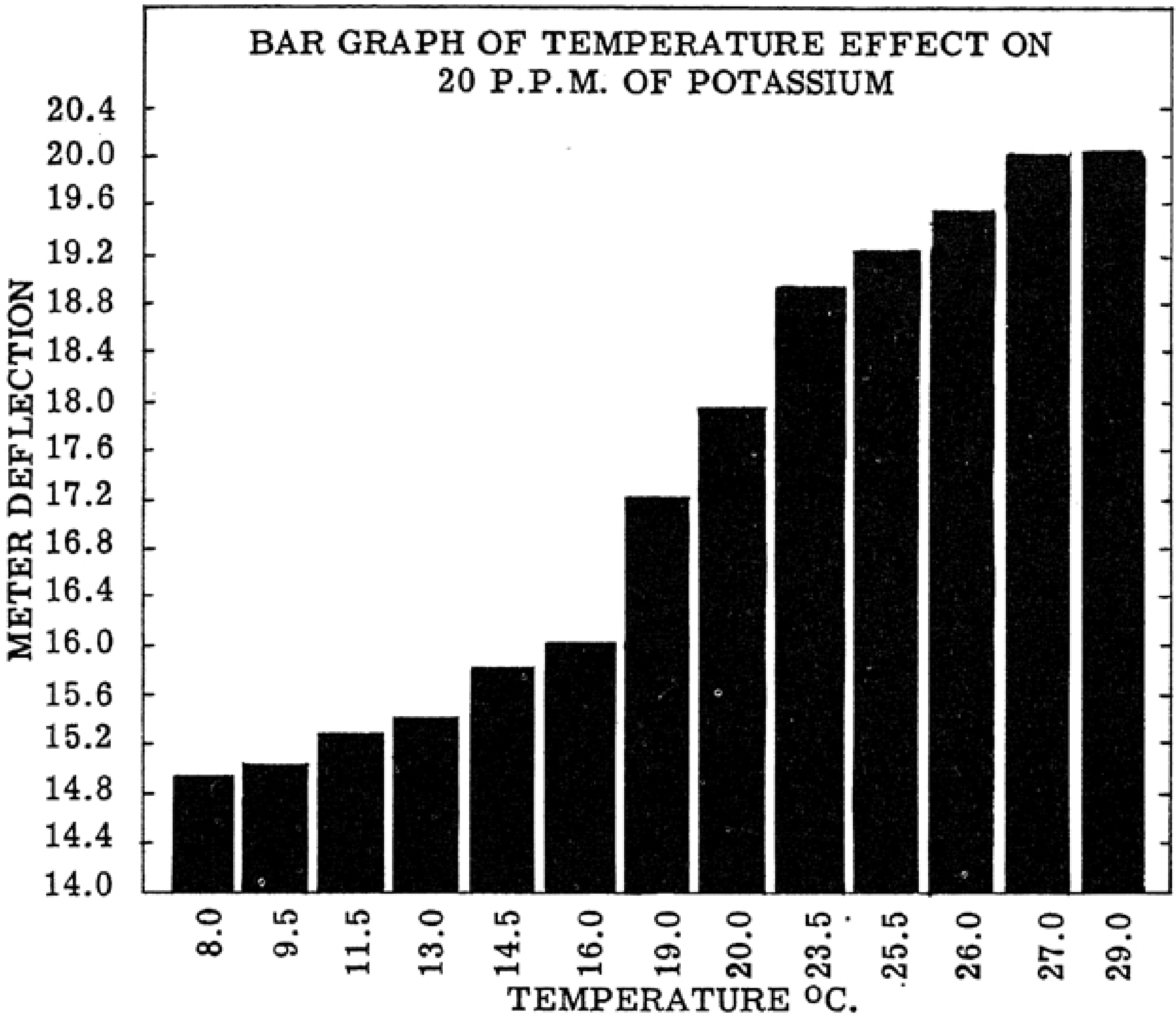


TABLE 15. EFFECT OF ASPIRATING SOLUTION TEMPERATURE ON THE METER DEFLECTION OF 20 P.P.M. OF POTASSIUM

Temperature °C.	Meter Deflection*
8	14.9
9.5	15.0
11.5	15.3
13.0	15.4
14.5	15.8
16.0	16.0
19.0	17.2
20.0	17.9
23.5	18.9
25.5	18.9
26.0	19.2
27.0	20.0
29.0	20.0

*A 20 p.p.m. standard solution of K was divided into two equal parts. One part was held at room temperature (29°C.) and the other was cooled to about 0°C. Readings were taken over a 40-minute period as the cooled solution warmed to room temperature. The photometer was set initially at a reading of 20.0 with the room temperature sample, and maintained at this reading during the experiment by repeated checking against this sample.

RECOVERY STUDIES ON SYNTHETIC SAMPLES

Synthetic Samples.

A series of 7 synthetic samples was prepared (Table 16) from a stock solution containing 10,000 p.p.m. of potassium from A.R. potassium nitrate. These samples were used to determine the effect of extraneous cations and anions on the emission intensity of potassium at levels of potassium normally encountered in commercial fertilizers. Amounts of potassium equivalent to the amounts found in 1.5058-gram samples of fertilizer containing 4, 8, 12, 16, 20, 40, and 60% of K_2O, respectively, were added to a boiling flask.

For example, a 4.00% K_2O commercial fertilizer contains the equivalent of 50 mg. of potassium in a 1.5058-gram sample. To obtain this amount of potassium, a 5 ml. aliquot of the 10,000 p.p.m. stock solution of potassium was added to the 250-ml. boiling flask. The other synthetic samples were prepared accordingly. Then, the ions normally found in commercial fertilizers, Ca^{++}, Mg^{++}, Na^{+}, NH_4^{+}, SO^{--}_4, PO^{---}_4, CO^{--}_3, Cl^{-}, etc., were added individually at various levels to the boiling flask. Aliquots of the "unprocessed" synthetic samples were then taken and diluted to the appropriate volumes as presented in the section "Analytical Method" and Table 16. Next they were atomized to determine the effect of the particular added cation or anion on the recovery of potassium. In one set of samples, all of the cations and anions were added to the synthetic samples at the same level as when added alone. This set was called the "composite sample".

To determine the effectiveness of the carbonate precipitation and ion exchange clean-up by the batch procedure in eliminating the diverse ions, an exact duplicate set of synthetic samples was prepared and processed through the entire analytical procedure. The flame results of the "processed and non-processed" synthetic samples were then compared. (See data, Tables 18 to 24.) Quantitative analyses for the interfering ions were made on the remaining portions of the aspirating solutions of the "processed samples" to determine the concentration of the ions remaining.

TABLE 16. PREPARATION AND COMPOSITION OF SYNTHETIC SAMPLES

Sample No.	Aliquot Drawn from Stock*	Mg. of K in 250-ml. Boiling Flask	Aliquot Volume-and Diluted to	Mg. of K in Aspirating Flask	P.P.M. of K in Aspirating Solution	Conversion Factor	% K_2O Present
1	5	50	25- 250	5	20	0.2	4.00
2	10	100	25- 250	10	40	0.2	8.00
3	15	150	25- 250	15	60	0.2	12.00
4	20	200	25- 500	20	40	0.4	16.00
5	25	250	25- 500	25	50	0.4	20.00
6	50	500	20-1000	40	40	1.0	40.00
7	75	750	20-1000	60	60	1.0	60.00

*The stock solution contained 10,000 p.p.m. of K from A.R. KNO_3.

Standards (Table 17).

Standards were prepared containing KNO_3 plus distilled water, with no added interfering ions. Five, 10, 15, 20, 25, 50, and 75-ml. aliquots of the 10,000 p.p.m. stock solution of KNO_3 were drawn and added to the 250-ml. boiling flasks. Then the further appropriate aliquots were drawn and diluted to volume (Table 16). These solutions were aspirated into the flame and compared against previously prepared standards of A.R. KNO_3. The solutions were in reality a second series of standards, the only difference being that the representative aliquots of the stock solutions were carried through the respective dilutions in the volumetric flasks as is customary in routine fertilizer analysis.

Blank Determination (Table 17).

Appropriate aliquots were drawn from the stock solution of 10,000 p.p.m. of K to give standards containing amounts of potassium equivalent to those found in 4, 8, 12, 16, 20, 40, and 60% K_2O commercial fertilizers. These samples were processed through the entire analytical method. Results are in Table 17, column 3.

Resin Blank (Table 17).

Five, 10, 15, 20, 25, 50, and 75-ml. aliquots of the 10,000 p.p.m. stock solution of K were placed in contact with 30 ml. of IR-4B-NO_3 anion exchange resin, allowed to stand one hour, agitated occasionally, filtered, made to volume, then aspirated into the flame. Results are given in Table 17, column 4.

Phosphate Interference Study (Table 18).

A stock solution of $(NH_4)_2HPO_4$ containing 26.9 g. per liter was prepared. Phosphate was added to each boiling flask equal in amount approximately to that present in a 1.5058-gram sample of commercial fertilizer containing 24% P_2O_5. A 25-ml. aliquot of the stock solution was added; this was equivalent to 671.8 mg. of $(NH_4)_2HPO_4$ or 361 mg. of P_2O_5.

Oxalate Interference Study (Table 19).

A 50-ml. volume of 4% solution of $(NH_4)_2C_2O_4 \cdot H_2O$ was added to each boiling flask. This is equivalent to 1600 mg. of $C_2O^{--}_4$ or to the amount normally added in the preparation of the official A.O.A.C. potash solution.

Sulfate Interference Study (Table 20).

Sulfate was added to each boiling flask equal to the amount in a 1.5058-gram sample containing 10% nitrogen as $(NH_4)_2SO_4$ and 10%

TABLE 17. EFFECT OF DILUTION, PROCESSING, AND RESIN CONTACT (BATCH) ON THE RECOVERY OF POTASSIUM

K_2O Present, %	K_2O Found, % Dilution Blank	Process Blank	Resin Blank
4.00	4.00	4.00	4.00
8.00	8.02	8.00	8.00
12.00	12.04	12.07	11.94
16.00	16.11	16.00	15.95
20.00	20.00	19.95	19.95
40.00	40.00	40.00	39.98
60.00	59.96	60.18	59.95

TABLE 18. EFFECT OF PHOSPHATE ON THE RECOVERY OF POTASSIUM

	Unprocessed		Processed	
K_2O Present, %	K_2O Found, %	Conc. of $PO_4^{\equiv}$ P.P.M.	K_2O Found, %	Conc. of $PO_4^{\equiv}$ P.P.M.
4.00	3.66	140	4.02	7.0
8.00	7.63	140	8.03	8.0
12.00	11.58	140	12.00	9.0
16.00	15.52	70	16.06	6.0
20.00	19.33	70	20.00	5.0
40.00	38.90	30	39.92	2.0
60.00	59.50	30	59.69	3.0

Phosphate was added to each boiling flask approximately equal in amount to that present in a 1.5058 - gram sample of commercial fertilizer containing 24% P_2O_5.

TABLE 19. EFFECT OF OXALATE ON THE RECOVERY OF POTASSIUM

	Unprocessed		Processed	
K_2O Present, %	K_2O Found, %	Conc. of $C_2O_4^{=}$ P.P.M.	K_2O Found, %	Conc. of $C_2O_4^{=}$ P.P.M.
4.00	4.15	640	4.17	131
8.00	8.22	640	8.10	88
12.00	12.21	640	12.12	76
16.00	16.15	320	16.30	49
20.00	20.33	320	20.00	38
40.00	40.00	130	40.27	16
60.00	60.00	130	60.15	14

Fifty ml. of a 4% solution of $(NH_4)_2C_2O_4 \cdot H_2O$ added to each boiling flask.

TABLE 20. EFFECT OF SULFATE ON THE RECOVERY OF POTASSIUM

	Unprocessed		Processed	
K_2O Present, %	K_2O Found, %	Conc. of $SO_4^{=}$ P.P.M.	K_2O Found, %	Conc. of $SO_4^{=}$ P.P.M.
4.00	3.76	225	4.06	0
8.00	7.95	225	8.22	0
12.00	11.80	225	12.00	0
16.00	15.74	110	16.00	0
20.00	19.84	110	19.90	0
40.00	38.91	45	40.14	0
60.00	59.26	45	60.00	0

Sulfate was added to each boiling flask equal to the amount in a 1.5058-gram sample containing 10% nitrogen as $(NH_4)_2SO_4$ and 10% K_2O as K_2SO_4.

K_2O as K_2SO_4. This amount was computed as follows:

150.58 mg. of $N_2 \approxeq$ 710.6 mg. of $(NH_4)_2SO_4$
150.58 mg. of $K_2O \approxeq$ 211.2 mg. of $(NH_4)_2SO_4$

Total = 921.8 mg. of $(NH_4)_2SO_4$
921.8 mg. of $(NH_4)_2SO_4$ = 558.6 mg. of SO^{--}_4

A stock solution of $(NH_4)_2SO_4$ containing 36.872 g. per liter was prepared. A 25-ml. aliquot of this solution, containing 558.6 mg. of SO^{--}_4, was added to each boiling flask.

Ammonium Chloride Interference Study (Table 21).

Chloride, as ammonium chloride, was added to the boiling flask of each synthetic sample, equivalent in amount to that present in a 1.5058-gram sample of fertilizer containing 16% K_2O added as KCl. A stock solution of NH_4Cl (10.944 g./l.) was prepared and a 25-ml. aliquot of this solution containing 273.6 mg. of NH_4Cl was added to each flask.

1.5058 g. sample x 0.16 = 0.2409 g. K_2O
240.9 mg. $K_2O \approxeq$ 381.39 mg. KCl
381.39 mg. KCl $\approxeq$ 273.6 mg, NH_4Cl

Magnesium Interference Study (Table 22).

Magnesium as $Mg(NO_3)_2 \cdot 6H_2O$ was added to the boiling flask of each synthetic sample, equivalent to the amount present in a 1.5058-gram sample of fertilizer containing 5% of magnesium. A stock solution of $Mg(NO_3)_2 \cdot 6H_2O$ (31.754 g./l.) was prepared, and a 25 ml. aliquot of this solution containing 793.85 mg. of $Mg(NO_3)_2 \cdot 6H_2O$ was added to each flask.

1.5058 g. sample x 0.05 = 75.29 mg. of Mg^{++}
75.29 mg. of $Mg^{++} \approxeq$ 793.85 mg. of $Mg(NO_3)_2 \cdot 6H_2O$

Calcium Interference Study (Table 23).

Calcium as $Ca(NO_3)_2 \cdot 4H_2O$ was added to the boiling flask of each synthetic sample, equivalent to the amount present in a 1.5058-gram sample of fertilizer containing 50% of $CaCO_3$. A stock solution of $Ca(NO_3)_2 \cdot 4H_2O$ (71 g./l.) was prepared, and a 25 ml. aliquot of this solution containing 1776.8 mg. of $Ca(NO_3)_2;4H_2O$ was added to each flask.

1.5058 x 0.50 = 752.9 mg. of $CaCO_3$
752.9 mg. of $CaCO_3 \approxeq$ 1776.8 mg. of $Ca(NO_3)_2 \cdot 4H_2O$

Composite Interference Study (Table 24).

A combination of all the interfering ions at levels which they were studied singly was added to the composite sample. The ions were $PO^{---}4$, $C_2O^{--}_4$, SO^{--}_4, Cl^-, Mg^{++}, and Ca^{++}.

TABLE 21. EFFECT OF AMMONIUM CHLORIDE ON THE RECOVERY OF POTASSIUM

	Unprocessed		Processed	
K_2O Present, %	K_2O Found, %	Conc. of NH_4Cl P.P.M.	K_2O Found, %	Conc. of NH_4Cl P.P.M.
4.00	3.92	110	4.12	0
8.00	7.95	110	8.00	10
12.00	11.97	110	11.92	4
16.00	16.00	55	16.00	0
20.00	19.92	55	20.00	8
40.00	40.11	20	40.00	0
60.00	60.14	20	60.00	0

TABLE 22. EFFECT OF MAGNESIUM ON THE RECOVERY OF POTASSIUM

	Unprocessed		Processed	
K_2O Present, %	K_2O Found, %	Conc. of Mg^{++} P.P.M.	K_2O Found, %	Conc. of Mg^{++} P.P.M.
4.00	4.00	30	4.00	30
8.00	8.00	30	8.00	29
12.00	11.84	30	11.88	31
16.00	15.84	15	16.00	15
20.00	19.89	15	19.72	15
40.00	39.92	7.5	40.12	7.4
60.00	59.83	7.5	60.00	7.5

TABLE 23. EFFECT OF CALCIUM ON THE RECOVERY OF POTASSIUM

	Unprocessed		Processed	
K_2O Present, %	K_2O Found, %	Conc. of Ca^{++} P.P.M.	K_2O Found, %	Conc. of Ca^{++} P.P.M.
4.00	4.02	120	4.12	5
8.00	7.95	120	8.00	5
12.00	12.00	120	11.92	8
16.00	16.14	60	16.00	2
20.00	20.00	60	20.00	3
40.00	39.75	25	40.00	2
60.00	60.00	25	60.00	2

TABLE 24. EFFECT OF COMPOSITE DIVERSE IONS ON THE RECOVERY OF POTASSIUM

		Processed					
			Concentration of, P.P.M.				
K_2O Present, %	Unprocessed K_2O Found, %	K_2O Found, %	$PO_4^{\equiv}$	Mg^{++}	$SO_4^{=}$	NH_4Cl	Ca^{++}
4.00	3.86	4.00	0	0	0	14	37
8.00	7.59	8.00	0	16	0	14	17
12.00	11.59	12.05	0	6	0	21	18
16.00	15.28	16.00	4	1	0	14	2
20.00	18.53	20.00	0	8	0	10	9
40.00	37.96	40.00	0	3	0	7	4
60.00	58.00	60.00	0	3	0	10.0	5

The following chemicals were added to the boiling flasks of the composite samples, equivalent in amount to that present in a 1.5058-g. sample of commercial fertilizer with the percentages of constituents as shown.

$(NH_4)_2HPO_4 \underset{\sim}{=} 24\%\ P_2O_5$
$(NH_4)_2SO_4 \underset{\sim}{=} 10\%\ N_2 + 10\%\ K_2O$
$Mg(NO_3)_2 \cdot 6H_2O \underset{\sim}{=} 5\%\ Mg$
$NH_4Cl \underset{\sim}{=} 16\%\ K_2O$
$CaCO_3 \underset{\sim}{=} 50\%\ CaCO_3$

PART IV

RESULTS AND DISCUSSION ON APPLICATION OF METHOD TO FERTILIZERS

Results obtained on eight 1956 A.O.A.C. collaborative samples and 23 commercial fertilizers by the flame method and the official A.O.A.C. gravimetric methods are presented in Tables 25 through 29. Because the proposed procedure utilizes ammonium carbonate to precipitate calcium and magnesium as insoluble carbonates from the sample solutions instead of ammonium oxalate as given in the A.O.A.C. methods, comparative data are also given on these two methods of solution preparation. Ammonium carbonate was preferred as the precipitant in the flame procedure over ammonium oxalate due to the ease in removing the excess carbonate as carbon dioxide by adjusting the pH to 5 with dilute nitric acid. Use of ammonium oxalate as given in the A.O.A.C. method is also satisfactory; the excess oxalate ion was effectively removed by resin columns of Amberlite IR-4B, Permutit-S, and DeAcidite. The effectiveness of other resins in removing oxalate was not investigated. Separate aliquots were drawn from the original sample solution for each sample prepared according to the 1956 instructions to the collaborators and analyzed by the flame and Perrin methods. Each value given in Tables 25 and 26 was obtained from an independently prepared sample solution; a gravimetric value in Table 26 corresponds to a flame value for the same solution in Table 25. A total of 64 independent analyses were made by each method.

Data in the following tables give the maximum variation, standard deviation, and difference in results between methods for each sample. Each value in Tables 25, 26, 27, 28 and 29 represents the result obtained on an original preparation of the sample solution.

Results obtained by the flame method, carbonate solution (Table 25) were positive with respect to the A.O.A.C. gravimetric method, carbonate solution (Table 26), by an average of +0.11% K_2O. Results were negative with respect to the A.O.A.C. gravimetric method, oxalate solution (Table 28), by -0.065% K_2O. The results represent an average of 64 determinations by the flame method and 32 by the A.O.A.C. gravimetric oxalate method.

The results of the flame method, oxalate solution (Table 27), were positive with respect to the A.O.A.C. gravimetric method, oxalate solution (Table 28), by +0.08% K_2O. An average of 32 determinations was made by each method.

The results obtained by the A.O.A.C. gravimetric method, carbonate solution (Table 26), were negative with respect to the A.O.A.C. gravi-

TABLE 25. PERCENT K_2O FOUND IN 1956 A.O.A.C. COLLABORATIVE SAMPLES BY PROPOSED FLAME METHOD

	% K_2O (Flame), Sample No. and Guarantee							
	1	2	3	4	5	6	7	8
Determination	10-10-10	Sulfate of Potash-Magnesia	4-16-16	3-9-27	23-21-17	5-10-5	5-20-20	0-0-60
1	10.91	22.73	16.06	25.66	16.40	4.98	19.59	62.90
2	10.76	23.00	16.31	25.53	16.81	4.98	19.69	62.74
3	10.97	23.16	16.40	25.91	16.73	5.00	19.67	62.82
4	10.86	23.00	16.64	26.14	16.59	5.00	19.78	62.70
5	10.97	22.88	16.35	25.50	16.68	5.00	19.56	
6	10.92	22.93	16.34	25.92	16.34	5.00	19.49	62.90
7	10.92	22.55	16.41	26.21	16.62	5.04	19.52	62.99
8	10.94	22.44	16.42	26.26	16.32	5.06	19.74	
Average - Flame (Carbonate Sol'n)	10.91	22.83	16.37	25.89	16.56	5.01	19.63	62.84
High	10.97	23.16	16.64	26.26	16.81	5.06	19.78	62.99
Low	10.76	22.44	16.06	25.50	16.32	4.98	19.49	62.70
Maximum Variation	0.21	0.72	0.58	0.76	0.49	0.08	0.29	0.29
Standard Deviation	0.065	0.23	0.15	0.28	0.17	0.027	0.098	0.10
Average A.O.A.C. Grav. Carbonate Sol'n (Table 26)	10.72	22.87	16.18	25.66	16.58	4.96	19.53	62.68
Difference Between Methods	+0.19	-0.04	+0.19	+0.23	-0.02	+0.05	+0.10	+0.16
Average Difference -- + 0.11%								
Average Standard Deviation -- ± 0.18								

TABLE 26. PERCENT K_2O FOUND IN 1956 A.O.A.C. COLLABORATIVE SAMPLES BY A.O.A.C. OFFICIAL METHOD--CARBONATE SOLUTION

	% K_2O (Grav.), Sample No. and Guarantee							
	1	2	3	4	5	6	7	8
Determination	10-10-10	Sulfate of Potash-Magnesia	4-16-16	3-9-27	23-21-17	5-10-5	5-20-20	0-0-60
1	10.66	23.00	16.18	25.83	16.61	4.94	19.66	62.90
2	10.64	23.03	16.25	25.70	16.75	4.93	19.68	62.73
3	10.77	23.00	16.20	25.78	26.59	4.95	19.68	62.92
4	10.78	23.01	16.25	25.68	16.71	4.93	19.60	62.82
5	10.83	22.88	16.18	25.38	16.35	4.99	19.46	62.44
6	10.68	22.70	16.08	25.73		4.98	19.37	62.39
7	10.77	22.73	16.20		16.45	5.00	19.45	62.57
8	10.60	22.61	16.12	25.49		4.95	19.36	62.63
Average - Grav. (Carbonate Sol'n)	10.72	22.87	16.18	25.66	16.58	4.96	19.53	62.68
High	10.83	23.03	16.25	25.83	16.75	5.00	19.68	62.92
Low	10.60	22.61	16.08	25.38	16.35	4.93	19.36	62.39
Maximum Variation	0.23	0.42	0.17	0.45	0.40	0.07	0.32	0.53
Standard Deviation	0.076	0.156	0.055	0.150	0.139	0.027	0.129	0.185
Average Standard Deviation -- ± 0.12								

TABLE 27. COMPARISON OF FLAME AND A.O.A.C. GRAVIMETRIC RESULTS ON 1956 A.O.A.C. COLLABORATIVE SAMPLES--OXALATE SOLUTION

	% K_2O (Flame), Sample No. and Guarantee							
Determination	1 10-10-10	2 Sulfate of Potash-Magnesia	3 4-16-16	4 3-9-27	5 23-21-17	6 5-10-5	7 5-20-20	8 0-0-60
1	11.03	23.11	16.56	26.16	16.46	5.06	20.00	62.79
2	10.92	23.05	16.72	26.30	16.72	5.06	19.84	62.94
3	10.94	23.36	16.52	26.30	16.31	5.11	19.94	62.84
4	10.86	23.23	16.63	26.27	16.61	5.09	20.18	62.68
5	11.00	22.96	16.30	25.91	16.54	5.00		
6	11.00	22.80	16.44	26.11	16.64	5.12		
Average - Flame (Oxalate Sol'n)	10.96	23.09	16.53	26.18	16.55	5.07	19.99	62.81
High	11.03	23.36	16.72	26.30	16.72	5.12	20.18	62.94
Low	10.86	22.80	16.30	25.91	16.31	5.00	19.84	62.68
Maximum Variation	0.17	0.56	0.42	0.39	0.41	0.12	0.34	0.26
Standard Deviation	0.043	0.176	0.134	0.139	0.133	0.040	0.102	0.094
Average A.O.A.C. Grav. (Oxalate Sol'n) Table 28	10.88	23.00	16.48	25.84	16.49	5.14	19.93	62.80
Difference Between Methods	+0.08	+0.09	+0.05	+0.34	+0.06	-0.06	+0.06	+0.01

Average Difference of Flame (Oxalate Sol'n) from A.O.A.C.--Oxalate Sol'n -- + 0.08

Average Standard Deviation of Flame - Oxalate Sol'n -- ± 0.108.

TABLE 28. COMPARISON OF A.O.A.C. GRAVIMETRIC AND FLAME RESULTS BY PROPOSED METHOD ON 1956 A.O.A.C. COLLABORATIVE SAMPLES

	% K_2O (A.O.A.C.) Grav., Sample No. and Guarantee							
	1	2	3	4	5	6	7	8
Determination	10-10-10	Sulfate of Potash-Magnesia	4-16-16	3-9-27	23-21-17	5-10-5	5-20-20	0-0-60
1	11.13	22.96	16.44	25.80	16.38	5.11	19.89	62.98
2	10.75	22.94	16.48	25.73	16.61	5.01	19.89	62.74
3	10.86	23.06	16.46	25.85	16.31	5.22	19.94	62.81
4	10.82	22.98	16.49	25.88	16.61	5.20	19.98	62.67
5	10.87	23.00	16.44	25.88	16.47	5.09		
6	10.83	23.06	16.54	25.88	16.56	5.19		
Average A.O.A.C. Grav. (Oxalate Sol'n)	10.88	23.00	16.48	25.84	16.49	5.14	19.93	62.80
Average of Proposed Flame Method (Table 25 Carbonate Sol'n)	10.91	22.83	16.37	25.89	16.56	5.01	19.63	62.84
Difference Between Methods	+0.03	-0.17	-0.11	+0.05	+0.07	-0.13	-0.30	+0.04
Average Difference of Flame (Carbonate Sol'n) from A.O.A.C. Grav. (Oxalate Sol'n) -- = -0.065								

metric method, oxalate solution (Table 28), by –0.17% K_2O. Average numbers of determinations were 64 and 32, respectively.

A comparison of the results obtained by the official gravimetric method, gravimetric method-carbonate solution, and flame method on 23 commercial fertilizers of widely different compositions showed the following average differences (Table 29).

Carbonate Solution.—Flame to A.O.A.C. gravimetric method: +0.01% K_2O.

Carbonate solution, flame Method to *oxalate solution,* A.O.A.C. gravimetric: _0.09% K_2O.

Carbonate solution, A.O.A.C. gravimetric method to *oxalate solution,* A.O.A.C. gravimetric method: –0.10% K_2O.

The average standard deviations were:

Method	*Solution*	*Standard Deviation, %*	*Number of Determinations*
Flame	Carbonate	±0.18	64
A.O.A.C. Gravimetric	Carbonate	±0.12	64
Flame	Oxalate	±0.11	32

Results obtained in the collaborative study on the 1956 potash referee samples as taken from the Associate Referee's report (2) are shown in Table 29A. The Missouri station was listed as collaborator number 19. In this investigation, the coefficient of variation for the "proposed flame method" for all samples was 1.74% as compared to 1.79% for the official gravimetric method, and the average standard deviation for all samples by the flame method was ±0.34 as compared to ±0.35 for the official gravimetric method. The following table from the Associate Referee's report (2) summarizes the average coefficient of variation by years for the official gravimetric and proposed flame methods.

Data and Source of Data		*Average Coefficient of Variation*	
		Gravimetric, %	*Flame, %*
Magruder	1953-54	1.79	2.10
A.O.A.C. Collaborative	1954	1.67	1.99
	1955	1.78	------
	1956	1.79	1.74

The average coefficient of variation of 1.74% for the "proposed flame method" for 1956 was lower than the coefficient for the other flame methods used in previous years, and was lower than the coefficient of variation for the A.O.A.C. gravimetric method in three of the four studies. Although the 1956 investigation by the collaborators was limited in number of analyses (about 500), this study showed that increased precision was gained by the removal of interfering ions and it also indicated that the "proposed flame method" compared quite favorably with the existing A.O.A.C. official gravimetric methods.

TABLE 29. COMPARISON OF OFFICIAL GRAV. METHOD, GRAV. METHOD-CARBONATE SOLUTION, AND PROPOSED FLAME METHOD ON COMMERCIAL FERTILIZERS OF DIFFERENT COMPOSITIONS

Sample No.	Guarantee*	% K_2O and Methods of Analysis							
		Proposed Flame			Average**	Gravimetric Carbonate Sol'n		Average**	Official*** Average
1	4-24-12	11.27	11.24	11.22	11.24	10.97	11.18	11.07	11.24
2	3- 9-27	16.71	16.48	16.56	16.58	16.34	16.48	16.41	16.84
3	4-24-12	10.31	10.12	10.02	10.15	10.20	10.16	10.18	10.13
4	8- 8- 8	8.25	8.05	8.02	8.11	8.10	8.26	8.18	8.27
5	4-12- 4	6.43	6.30	6.40	6.38	6.31	6.38	6.35	6.19
6	2-12- 6	6.93	6.86	6.91	6.90	6.82	6.84	6.83	6.85
7	4-16-16	15.80	15.96	15.90	15.89	15.80	15.85	15.83	15.62
8	6-24-24	21.58	21.53	21.37	21.49	21.52	21.55	21.54	21.63
9	5-10- 5	7.28	7.24	7.28	7.27	7.19	7.35	7.27	7.34
10	4-10- 6	6.11	6.17	6.24	6.17	6.02	6.26	6.14	6.22
11	10-10-10	10.08	10.13	10.13	10.11	9.93	10.12	10.03	10.28
12	12-24-12	11.35	11.33	11.24	11.31	11.15	11.28	11.22	11.57
13	3- 9-20	19.56	19.50	19.60	19.55	19.42	19.57	19.50	19.67
14	3-12-12	10.28	10.42	10.41	10.37	10.29	10.29	10.29	10.37
15	4-16-16	10.54	10.56	10.58	10.56	10.77	10.61	10.69	10.60
16	6-12-12	6.50	6.42	6.56	6.49	6.46	6.50	6.48	6.66
17	5-20-20	17.10	16.93	16.76	16.93	16.92	16.97	16.95	17.29
18	5-15-30	26.01	25.88	25.76	25.88	25.92	26.02	25.97	26.44
19	0-20-20	18.27	18.16	18.20	18.21	18.20	18.33	18.27	18.41
20	4-12- 4	3.78	3.67	3.70	3.72	3.68	3.79	3.74	3.72
21	4-12- 4	3.56	3.53	3.50	3.53	3.49	3.55	3.52	3.58
22	8- 8- 8	7.36	7.18	7.24	7.26	7.29	7.24	7.27	7.42
23	23-21-17	16.60	16.35	16.48	16.48	16.74	16.34	16.54	16.35

Average Difference of Proposed Flame from Gravimetric (Carbonate Solution) + 0.01

Average Difference of Proposed Flame from Official Gravimetric (Oxalate Solution) -0.09

Average Difference of Gravimetric (Carbonate Solution) from Official Gravimetric - 0.10

*Samples chosen were "deficient" commercial fertilizers.

**Duplicate aliquots were drawn from the flame carbonate solution for the gravimetric analysis.

***A.O.A.C. Official Method, oxalate solution, 2 to 6 determinations for each sample.

TABLE 29A. COMPARISON OF THE AVERAGE % K_2O BY THE GEHRKE FLAME, A.O.A.C., AND VOLUMETRIC METHODS FOR 1956

(Taken from A.O.A.C. Associate Referee's 1956 Report)

Collaborator No.	Avg. No. Det.	1			2			3			4		
		Flame	A.O.A.C.	Vol.	Flame	A.O.A.C.	Vol.	Flame	A.O.A.C.	Vol.	Flame	A.O.A.C.	Vol.
1	2		10.90			22.83			16.56			26.12	
2	4	10.92	10.85	10.92	22.75	23.18	23.15	16.29	16.35	16.65	25.88	25.81	26.16
3	3	10.82	10.53		23.17	22.41	22.80	16.33	16.10	16.19	25.73	25.30	
4	1-3	10.84	10.94	11.06	23.00	23.27	23.24	16.44	16.35	16.68	25.80	25.76	26.05
5	3	11.09	11.09	11.49	23.10	23.30	23.81	16.65	16.50	17.59	26.38	25.97	26.74
6	4		10.63	10.23		22.51	22.40		16.68	16.04		25.94	25.73
7	2	10.83	11.10	10.72	23.44	23.27	22.11	16.77	16.99	16.25	26.00	26.42	25.17
8	3	10.63	10.78		22.28	23.16		16.13	16.23		25.97	25.96	
9	4	10.90	10.85		23.16	23.22		16.43	16.46		25.99	25.92	
11	1-2	11.03		10.96	23.50		23.08	16.36		16.55	25.68		25.91
12	1-4	10.62	10.57	10.52	23.00	23.06	22.68	16.13	16.11	16.09	25.56	25.73	25.37
13	4	10.88	10.94	10.85	23.12	23.22	22.98	16.33	16.42	16.46	25.84	25.91	25.83
14	4	10.75	10.78		23.48	23.44		16.88	16.52		26.45	26.20	
15	3	10.83	10.30		22.67			16.33	15.56		25.67	24.93	
16	3	11.09			23.44			16.88			26.38		
17	2		10.95	11.07		23.55	23.25		16.45	16.54		26.08	25.65
18	4	11.16	10.85		23.48	23.08		16.61	16.28		26.31	25.88	
19	4	10.90	10.73		22.94	22.98		16.28	16.20		25.65	25.67	
20	4	10.95	10.98	11.11	22.98	23.59	23.45	16.05	16.52	16.58	26.09	24.72	25.95
High		11.16	11.10	11.49	23.48	23.59	23.81	16.88	16.99	17.59	26.45	26.42	26.74
Low		10.62	10.30	10.52	22.28	22.41	22.11	16.05	15.56	16.19	25.56	24.72	25.17
Max. Var. in Method		.54	.80	.97	1.20	1.18	1.70	.83	1.43	1.40	.89	1.70	1.57
Max. Var. from Av. ±		+.27	-.51	+.60	-.81	-.72	-.88	+.47	-.80	+1.05	+.49	-1.06	+.88
Average		10.89	10.81	10.89	23.09	23.13	22.99	16.41	16.36	16.54	25.96	25.78	25.86
Std. Dev.		.15	.22	.30	.34	.32	.48	.25	.30	.42	.29	.43	.27
Coef. Var.		1.4	2.0	2.7	1.4	1.4	2.1	1.5	1.8	2.5	1.1	1.6	1.0

TABLE 29A -- (Continued)

Collab-orator No.	Avg. No. Det	5			6			7			8		
		Flame	A.O.A.C.	Vol.	Flame	A.O.A.C.	Vol.	Flame	A.O.A.C.	Vol.	Flame	A.O.A.C.	Vol.
1	2		16.44			5.0			19.02			63.32	
2	4	16.70	16.71	16.69	5.09	5.03	5.42	19.53	19.60	20.23	62.75	63.41	63.43
3	3	16.71	16.59	16.93	4.81	4.79		19.98	19.23		63.07	61.08	63.07
4	1-3	16.90	17.03	17.24	5.05	5.03	5.24	19.70	19.89	20.06	62.50	63.11	63.25
5	3	17.19	17.16	17.75	4.92	5.13	5.89	19.20	19.81	20.78	62.13	63.29	63.13
6	4		16.10	16.23		5.09	4.63		20.24	19.58		63.45	59.95
7	2	17.08	17.12	16.12	4.72	5.07	4.85	20.30	20.30	19.55	64.75	64.10	64.67
8	3	18.03	18.35		5.14	5.13		19.71	19.57		62.47	63.27	
9	4	16.88	16.96		4.97	5.23		20.05	19.86		63.05	62.97	
11	1-2	16.90		16.94	5.10		5.25	20.20		20.17	62.75		62.75
12	1-4	16.71	16.67	16.56	4.75	5.12	5.00	19.21	19.57	19.65	61.50	62.94	62.00
13	4	17.01	17.01	16.89	4.89	4.98	5.02	19.69	19.75	19.61	63.03	63.07	63.09
14	4	17.26	17.44		5.21	5.13		19.91	20.08		63.38	63.29	
15	3	16.58	16.14		4.95	4.96		20.06			60.20		
16	3	16.23			4.95			19.88			62.88		
17	2		17.03	17.14		5.04	5.32		20.03	19.90		63.20	63.04
18	4	17.24	17.02		5.21	5.12		20.18	19.54		64.48	63.03	
19	4	16.66	16.58		4.99	4.95		19.63	19.62		62.72	62.75	
20	4	16.68	16.79	17.14	5.20	4.90	5.24	20.02	19.89	19.89	64.55	63.04	63.15
High		18.03	18.35	17.75	5.21	5.23	5.89	20.30	20.30	20.78	64.75	64.10	64.67
Low		16.23	16.14	16.12	4.72	4.79	4.63	19.20	19.02	19.55	60.20	61.08	59.95
Max. Var. in Method		1.80	2.24	1.63	.49	.44	1.26	1.10	1.28	1.23	4.55	3.02	4.72
Max. Var. from Av. ±		+1.11	+1.46	+.87	-.27	+.25	+.70	+.63	+.73	+.84	-2.44	-2.00	-2.90
Average		16.92	16.89	16.88	4.99	5.04	5.19	19.83	19.75	19.94	62.64	63.08	62.85
Std. Dev.		.40	.51	.46	.16	.10	.34	.33	.34	.38	.78	.60	1.105
Coef. Var.		2.3	3.0	2.7	3.2	1.99	6.5	1.66	1.72	1.9	1.2	.95	1.6

PART V
EFFICIENCY OF DIFFERENT ION EXCHANGE RESINS

Twelve different ion exchange resins were selected from four commercial companies. Four of the resins were strongly basic, six were classed as acid adsorbents, one of intermediate basicity, and one contained both strongly and weakly basic functional groups. The resins are listed in Table 30 along with their characteristics. Both batch (Table 31) and column techniques (Table 32) were used to determine the effectiveness of these resins in removing phosphate ions from an aliquot of a sample solution.

TABLE 30. CHARACTERISTICS* OF VARIOUS ANION EXCHANGE RESINS

Name of Ion Exchange Resin	Type	Form	Active Group	Total Exchange Capacity Meq./ml. wet resin	Effective pH Range
Dowex 1	Strongly basic	Beads	Trimethyl Benzyl Ammonium	1.33	0-14
Amberlite IR-45	Weakly basic	Beads	Polyamine	2.0	0- 7
Dowex 3	Weakly basic	Beads	Polyamine	2.5	0- 7
Amberlite IRA-400	Strongly basic	Beads	Quaternary Ammonium	1.0	0-12
Duolite A-40	Strongly basic	Beads	Quaternary Ammonium Groups	0.8	0-14
Duolite A-41	Bifunctional	Beads	Quaternary Ammonium Groups and tertiary amines	0.8	0-12
Duolite A-6	Weakly basic	Granules	Tertiary amines	2.0	0- 7
Duolite A-7	Weakly basic	Granules	Pr., Sec., and Tert. amines	1.5	0- 7
Duolite A-70	Intermediate basic	Granules	Tertiary amines	2.0	0- 7
Amberlite IR-4B	Weakly basic	Granules	Polyamine	3.0	0- 7
DeAcidite	Weakly basic	Granules	Aliphatic amine	1.0	0-12
Permutit-S	Strongly basic	Beads	Quaternary Ammonium	0.8	0-14

*This information was obtained from the descriptive literature supplied by the respective companies (22, 8, 21, 7).

TABLE 31. RESIN CONTACT TIME STUDIES ON REMOVAL OF PHOSPHATE WITH DIFFERENT ANION EXCHANGE RESINS
BATCH METHOD

	Method of Agitation		
	Intermittent 15 Min.	Intermittent 24 Hrs.	Continuous 15 Min.
	Mg. of P_2O_5* in Resin Contacted Samples		
Dowex 1	12.43	11.16	7.68
Duolite A-41	7.00	5.45	5.05
Duolite A-7	4.85	5.02	2.58
DeAcidite	5.50	4.50	6.90
Permutit-S	5.00	4.50	6.00
Amberlite IR-4B	1.55	1.25	1.50

Each 25-ml. sample aliquot initially contained 42.35 mg. of P_2O_5 prior to contact with 30 ml. of damp resin in the nitrate form.

*Each value is an average of two independent determinations.

The pH's of the sample solutions after 15 minutes of contact with the resins were: Dowex 1-4.7, Duolite A-41-2.1, Duolite A-7-2.5, DeAcidite-2.7, and Permutit-S-2.7. Note that Amberlite IR-4B was the only resin of the group that removed the phosphate to a level which would not interfere in subsequent flame analysis for potassium.

Thirty milliliters of resin were used in all of the batch studies and a column of resin 11 inches long, 1 inch in diameter, was used in the column work. Each column contained approximately 135 ml. of wet resin in the nitrate form. The resins were regenerated to the nitrate form as given in the section "Analytical Method" under regenerating procedure.

A stock solution of A.R. KNO_3 containing 6.206 g./100 ml. was prepared. This solution (A) contained 2400 mg. of K/100 ml. or 24,000 p.p.m. A 25-ml. aliquot (600 mg. of K) of this stock solution (A) was placed in a 2-liter flask and diluted to volume (300 p.p.m.—Solution B). Then a 100-ml. aliquot of Solution B (30 mg. of K) was placed in a 1 liter flask and made to volume (30 p.p.m.—Solution C). This final standard potassium, Solution C was used as the reference potassium standard for all studies on sample aliquots passed through the different ion exchange columns.

Another stock solution was prepared from which all aliquots were taken and passed through the 12 different ion exchange columns. Fifty ml. of Solution A (1200 mg. of K.) were placed in a 4-liter volumetric flask, 12.602 g. of $(NH_4)_2HPO_4$ were also added, and the solution was made to volume. This solution contained 7.5 mg. of K, and 42.35 mg. of P_2O_5 in each 25-ml. aliquot. Ten 25-ml. aliquots of this solution were passed consecutively through each anion exchange column. The flow rate was 7 ml./minute for the aliquot and the first three washes, each about 25 ml. The flow rate was then increased to 10 to 15 ml. per minute for the remainder of the run and the effluent was collected in a 250-ml. volumetric flask. In each series and for each resin, flasks 1 through 4 were filled to 250 ml.

TABLE 32. RESIN EXHAUSTION STUDY AND COMPLETENESS OF REMOVAL OF PHOSPHATE BY COLUMNS OF VARIOUS ION EXCHANGE RESINS

Aliquot No. Through Column	P.P.M. of P_2O_5 in Aspirating Solutions											
	Amb. IR-45	Dow. 3	Duo. A-6	Amb. IRA-400	Duo. A-40	Duo. A-70	Dow. 1	Per-S	Duo. A-41	DeA	Duo. A-7	Amb. IR-4B
1	5.5	5.5	3.0	0.0	0.0	1.5	0.0	0.0	0.0	0.0	0.0	0.0
2	10.0	11.0	22.5	trace	3.0	2.5	0.0	trace	0.0	0.0	0.0	0.0
3	18.5	12.5	36.0	11.5	10.5	9.0	0.0	trace	0.0	0.0	0.0	0.0
4	24.0	22.5	35.0	24.0	17.5	22.5	3.5	trace	0.0	trace	0.0	0.0
5	21.5	17.5	28.5	37.0	26.0	17.5	5.5	2.0	0.0	2.0	0.0	0.0
6	25.5	21.0	30.5	34.0	29.5	30.0	7.5	2.4	2.0	2.0	0.0	0.0
7	24.0	20.6	38.8	56.4	48.2	39.0	21.6	3.2	2.0	2.2	1.2	0.0
8	30.8	28.4	43.6	67.2	54.6	52.4	32.6	3.2	1.7	2.8	1.6	0.0
9	32.2	30.0	52.6	78.4	63.0	54.0	39.6	4.0	2.8	3.5	1.7	0.0
10	35.0	33.4	50.0	83.2	75.2	60.8	50.4	5.0	4.4	3.8	2.0	0.0
B.T.P.	2	2	2	3	3	3	6	>10	>10	>10	>10	26

Ten consecutive 25 ml. aliquots were passed through each column of resin. Each aliquot contained 7.5 mg. of K and 42.35 mg. of P_2O_5. Thus, if each initial sample were made to a volume of 250 ml. it would contain 30.0 p.p.m. of K and 169.4 P.P.M. of P_2O_5. After passing the aliquots through the columns the effluents were diluted to a final volume of 250 ml.

Amberlite IR-4B, Duolite A-7, DeAcidite, Duolite A-41, and Permutit-S were the most effective resins in the order given. Dowex 1 was fairly satisfactory.

The heavy black line marks the B.T.P. (break through point of phosphate).

by passing distilled water through the column. For flasks 5 through 10 of each series only 150 to 175 ml. of water were passed through the column. Thus, if none of the potassium or P_2O_5 were retained by the resin, each receiving flask should contain 7.5 mg. or 30 p.p.m. of potassium, and 169.4 p.p.m. of P_2O_5. It was shown that all of the potassium was quantitatively recovered from the columns with 150 to 175 ml. of wash water. The resin polymer is positively charged and thus prevents absorption of potassium within the resin particles. Also, all of the aliquots passed through the resin columns were identical and were prepared from the same original stock solution (A), as was reference standard "C".

The first six sample effluents were aspirated into the flame and their potassium content determined by comparing against reference standard "C." The phosphate remaining in each flask was determined by the A.O.A.C. method (3). The data are in Tables 32 and 33. Before placing the regenerated resins in the columns they were rinsed with distilled water until free of sodium ions as determined by the flame test. The pH of each aliquot and washings through each resin was determined. Table 34 gives these pH's. The pH of the effluent of the strongly basic resins was approximately 3.5, and for the weakly basic resins about 2.5. Some mineral acidity leached from the weakly basic resins on washing. Duolite A-70 was the only resin that continuously lost color on repeated rinsing.

Phosphate and sulfate are the anions which most seriously affect the emission intensity of potassium. The proper choice of exchange resin, with a high exchange capacity for these anions, will determine the efficiency of clean-up of the sample aliquot. Tables 32 and 33 show that the different resins vary significantly in their capacity to remove phosphate. The effectiveness of an ion exchange resin is dependent upon a number of factors, e.g. pH, exchange capacity, density, porosity, functional exchange group, charge and mobility of ion in solution, column length, and flow rate.

After considering results of interference studies concerning the effect of phosphate on potassium emission (Part III), the Break-Through-Point was set at 5.5 p.p.m. of P_2O_5 in the aspirating solution. This is the maximum amount of phosphate permissible in the aspirating solution under the conditions of the experiments set down in this manuscript. The heavy black line in Table 32 marks the B.T.P. for phosphate. The B.T.P. was arbitrarily defined as the point at which the resin no longer was effective in removing phosphates and the aspirating solutions contained more than 5.5 p.p.m. of P_2O_5. The B.T.P. was reached for some resins after only one or two aliquots were put through the column; thereby making these resins unsatisfactory for column or batch techniques. Five of the resins had a B.T.P. greater than 10, and the B.T.P. for Amberlite IR-4B had not been

TABLE 33. METER DEFLECTION OF THE ASPIRATING SOLUTIONS OF THE FIRST SIX ALIQUOTS THROUGH THE RESIN COLUMNS LISTED IN TABLE 32

Aliquot No. Through Column	Meter Deflection											
	Amb. IR-45	Dow. 3	Duo. A-6	Amb. IRA-400	Duo. A-40	Duo. A-70	Dow. 1	Per-S.	Duo. A-41	DeA	Duo. A-7	Amb. IR-4B
1	25.0	24.9	24.9	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
2	24.8	24.5	24.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
3	24.4	24.0	23.1	24.9	24.8	24.3	25.0	25.0	24.9	25.0	25.0	25.0
4	24.1	23.9	23.2	24.1	24.3	23.8	25.0	25.0	24.9	25.0	25.0	25.0
5	24.3	24.2	23.2	23.4	23.9	23.6	25.0	25.0	25.0	25.0	25.0	25.0
6	24.1	23.8	23.4	23.1	23.6	23.8	24.7	25.0	24.9	25.0	25.0	25.0
B.T.P.	2	2	2	3	3	3	6	>10	>10	>10	>10	26

The instrument was adjusted to give a meter deflection of 25.0 for a 30 p.p.m. K standard containing no P_2O_5. Stock Solution C was used as the reference standard for all comparisons.

Each 25-ml. sample aliquot that was passed through the different columns initially contained 7.5 mg. of K and 42.35 mg. of P_2O_5 and was diluted to a total final volume of 250 ml. (30 p.p.m. of K).

Note that where the B.T.P. line in Table 32 is transposed on Table 33 it indicates the approximate point at which the meter deflection for K is significantly depressed.

TABLE 34. pH OF EFFLUENTS FROM COLUMNS OF DIFFERENT ANION EXCHANGE RESINS

Aliquot No.	Amb. IR-45	Dow. 3	Duo. A-6	Amb. IRA-400	Duo. A-40	Duo. A-70	Dow. 1	Per-S	Duo. A-41	DeA	Duo. A-7	Amb. IR-4B
1	2.2	2.1	2.0	3.7	3.4	2.3	3.6	1.9	1.7	2.2	2.2	2.7
2	2.2	2.1	2.0	3.6	3.3	2.3	3.5	2.1	1.7	2.3	2.2	2.7
3	2.2	2.1	2.1	3.6	3.3	2.4	3.4	2.1	1.9	2.4	2.2	2.7
4	2.3	2.2	2.1	3.6	3.3	2.4	3.4	2.3	1.9	2.4	2.3	2.7
5	2.4	2.4	2.4	3.8	3.5	2.6	3.7	2.3	2.1	2.5	2.5	2.7
6	2.5	2.4	2.3	3.7	3.6	2.6	3.7	2.5	2.2	2.6	2.6	2.7
7	2.4	2.3	2.3	3.6	3.3	2.6	3.6	2.6	2.1	2.7	2.4	2.7
8	2.4	2.3	2.3	3.6	3.3	2.6	3.6	2.6	2.1	2.8	2.4	2.7
9	2.4	2.4	2.4	3.6	3.3	2.6	3.6	2.6	2.2	2.7	2.4	2.7
10	2.4	2.4	2.4	3.6	3.4	2.7	3.6	2.6	2.2	2.6	2.4	2.7
pH of water on washed resin regenerated in nitrate form												
	2.5	2.5	2.1	4.5	4.9	2.3	3.8	2.4	2.5	2.6	2.3	2.4

All pH values were obtained with a Beckman Model G instrument.

No difficulties were encountered in washing Dowex 1, Amberlite IRA-400, and Duolite A-40 free of excess acid or base. The others leached some mineral acidity on continued washing.

reached after the passage of 26 aliquots. Thus, an 11 x 1 inch column of Amberlite IR-4B effectively removed 26 x 42.35 = 1101.1 mg. of P_2O_5. Any resin with a B.T.P. of 10 or greater would be ideal for removal of interfering anions by the column method. The following resins were considered satisfactory in the order of their effectiveness: Amberlite IR-4B, Duolite A-7, DeAcidite, Duolite A-41, and Permutit-S.

Data are presented in Table 33 giving the meter deflection values for each of the first 6 effluent solutions from the 12 different ion exchange resin columns. The instrument was adjusted to give a meter deflection of 25.0 for a potassium standard of 30.0 p.p.m. It will be observed that when the concentration of P_2O_5 in the aspirating solutions exceeded 5.5 p.p.m. that a significant suppression of the meter deflection values occurred.

Fifty milliliters of a saturated ammonium oxalate solution were diluted to 300 ml. and passed through an 11 x 1 inch column of Amberlite IR-4B-NO_3. The effluent was collected in 10 separate 30 ml. portions and each was analyzed quantitatively for oxalate. No oxalate was found in any of the effluent solutions. This experiment was repeated with columns of Permutit-S and DeAcidite resins. The oxalate ion was completely removed. Thus, each of the above resin columns quantitatively removed approximately 32 milliequivalents of ammonium oxalate (abuot 2.00 g.). The exchange capacity of the resin was not reached. This experiment represents the amount of oxalate that one would find in 10 separate aliquots from solutions of fertilizer samples. The total exchange capacity of the columns are: Amberlite IR-4B-300, Permutit-S-110, and DeAcidite-135 meqs.

The data in Table 35 confirm the previous findings on column removal of extraneous anions and quantitative recovery of potassium from the columns. An alternate ion-exchange column technique has been presented in Part I, Analytical Method.

TABLE 35. COMPARISON OF RESULTS OBTAINED ON 1956 A.O.A.C. COLLABORATIVE SAMPLES BY COLUMN AND BATCH METHODS OF ANION REMOVAL WITH IR-4B-NO_3

		Flame K_2O, % Found					
Sample No.	Guarantee	Column Method				Average Column Method	Average Batch Method (Table #25)
1	10-10-10	11.00	10.92	10.72	10.94	10.90	10.91
2	Sulfate of Potash-Magnesia	22.76	22.82	22.58	22.64	22.70	22.83
3	4-16-16	16.40	16.25	16.41	16.51	16.39	16.37
4	3- 9-27	25.60	25.88	25.85	25.91	25.81	25.89
5	23-21-17	16.51	16.27	16.56	16.72	16.52	16.56
6	5-10- 5	5.02	5.06	5.02	5.04	5.04	5.01
7	5-20-20	19.68	19.68			19.68	19.63
8	0- 0-60	62.84	62.84	63.00		62.89	62.84
		Average of Averages				22.49	22.51

SUMMARY

The major objectives of this investigations were: (a) To develop a simple, rapid, and accurate flame photometric method for the determination of potassium in commercial fertilizers. (b) To apply the principles of ion exchange in cleaning up the aspirating solution and in this way obviate the effects of extraneous anions on the emission intensity of potassium. (c) To study quantitatively, under specified conditions, the effect of the common interfering cations and anions at different concentrations on the emission intensity of potassium in standards, and on the recovery of potassium from synthetic samples.

Flame Photometric Method.

The method described in Part I, involving removal of interfering anions from the sample solution by ion exchange and chemical precipitation of cations as insoluble carbonates, proved simple, rapid, and precise, and compared in accuracy with official A.O.A.C. gravimetric methods. The method offers the following advantages: (1) Interference from anions is eliminated. (2) The total salt content of the aspirating solution is less than for techniques which use "radiation buffers;" this produces better atomizer performance and greater meter stability. (3) The atomized solution is on the acid side (pH of ca 2.5), which aids in keeping the atomizer clean. (4) With the recommended sample weight, aliquots, and dilutions the concentration of potassium in the atomized solutions is in the 20 to 60 p.p.m. range. In this range the meter deflection-concentration curve was linear or nearly so, and for each increment of 5 p.p.m. of potassium there was a change of 4 to 5 meter deflection units; whereas, at higher levels of potassium (65 to 100 p.p.m.) the instrument response was normally 3.2 to 2.8 units for each 5 p.p.m. increment of potassium. (5) With the recommended aliquots and dilutions the concentration of sodium in the aspirating solution was 1 to 2 p.p.m.; at this concentration, little effect was observed on the emission of potassium. (6) The sample aspirating solution has been cleaned up; is a simple system and was compared to a standard containing only potassium nitrate and no other added substances. (7) The excess ammonium carbonate precipitant is easily changed to ammonium nitrate and the carbonate anion is removed as carbon dioxide.

A "line segment" technique for reading the concentration of potassium from the working curve is described in Part I. The "line segment" is merely the position of a small part of the standard curve at the moment the sample is read. Thus, changes in air, fuel, oxygen pressure, atomizer performance, instrument drift, etc., become of less importance.

The flame method employing anion exchange resins to remove extraneous ions has been used for three years in the Missouri Experiment Station chemical laboratories. Approximately 10,000 routine determinations were made on commercial fertilizers with an accuracy comparable to that noted in Table 29.

An alternate ion exchange column method for anion removal is described. A detailed description is given of the column specifications, "self-feeder" flask, and laboratory assembly of a rack of columns for routine work.

Interference Studies

The emission intensity of potassium was significantly depressed by the following substances at the levels indicated. Phosphate—10 p.p.m.; sulfate—20 p.p.m.; temperature— a -3° C differential from the corresponding standard.

The emission intensity of potassium was significantly enhanced by the following substances at the levels indicated. Oxalate—20 to 4000 p.p.m. (depressed above 4000 p.p.m.); NH_4Cl—200 p.p.m.; carbonate—above 100 p.p.m.; calcium—20 p.p.m.; sodium—5 to 10 p.p.m.; formaldehyde—5 ml. of a 38% solution in a 500 ml. flask; temperature—a +3° C differential from the corresponding standard.

The emission intensity of potassium was not altered by the following substances at the levels indicated. Nitrate—2000 p.p.m.; magnesium—500 to 1000 p.p.m.; urea—1000 p.p.m.

Carbonate significantly enhanced the meter deflection of potassium at levels greater than 100 to 5000 p.p.m. However, the carbonates were removed in the proposed method when the sample solutions were adjusted to a pH of 5.

The emission intensity of potassium was not significantly changed by nitrate, added as NH_4NO_3, at levels of 100 to 2000 p.p.m. of NO^-_3 to potassium standards of 20, 30, 40, 50, 60, and 70 p.p.m. Identical standard curves were obtained from standards prepared with reagent grade KCl and KNO_3.

Comparison of Results with A.O.A.C. and Flame Methods

Carbonate Solution.—Flame to A.O.A.C. gravimetric: +0.11% K_2O. (64 determinations by each method.)

Carbonate solution, flame to *oxalate solution,* A.O.A.C. gravimetric method: -0.065%. (Flame—64 determinations; A.O.A.C.—32.)

Oxalate Solution.—Flame to A.O.A.C. gravimetric: +0.08% K_2O. (32 determinations by each method.)

Carbonate solution, A.O.A.C. gravimetric to *oxalate solution,* A.O.A.C. gravimetric: -0.17% K_2O. (carbonate—64 determinations; oxalate—32)

A comparison of the results obtained by the official gravimetric method; official gravimetric, carbonate solution; and flame method on 23 commercial fertilizers of widely different compositions showed the following average differences.

Carbonate Solution.—Flame to A.O.A.C. gravimetric method: +0.01% K_2O.

Carbonate solution, flame method to *oxalate solution,* A.O.A.C. gravimetric: -0.09% K_2O.

Carbonate solution, A.O.A.C. gravimetric method to *oxalate solution,* A.O.A.C. gravimetric method: -0.10% K_2O.

The following average standard deviations were obtained for the flame and gravimetric methods.

Method	*Solution*	*Average Standard Deviation*	*Determinations*
Flame	Carbonate	±0.18	64
A.O.A.C. Gravimetric	Carbonate	±0.12	32
Flame	Oxalate	±0.11	32

Batch and Column Exchange Removal of Interfering Ions

Resin contact time batch studies on the removal of PO_4^{---} by different anion exchange resins with intermittent agitation for 15 minutes showed that 5 to 20 p.p.m. of phosphate remained in the aspirating solution. In order, the most effective resins were: Amberlite IR-4B, Duolite A-7, DeAcidite, and Permutit-S.

Oxalate ions were effectively removed with an 11 x 1 inch column of Amberlite IR-4B, Permutit-S, and DeAcidite resins from solutions prepared by the official A.O.A.C method. Thus, ammonium oxalate, as recommended by the A.O.A.C., may be used instead of ammonium carbonate as the precipitant.

The following anion exchange resins are listed in the order of their effectiveness in removing phosphate anions: Amberlite IR-4B, Duolite A-7, DeAcidite, Duolite A-41, Permutit-S, and Dowex 1. The studies were conducted with resin columns 11 inches long and 1 inch in diameter. These resins, with the exception of Dowex 1, removed nearly all of the phosphate from 10 sample aliquots (42.35 mg. of P_2O_5 in each aliquot) passed through a single column at a flow rate of 4 to 7 ml. per minute. With a setup of 12 columns, 12 aliquots can be processed in 25 minutes.

CONCLUSIONS

A number of different analytical approaches have been published on flame photometry to gain increased sensitivity, precision, and to correct for extraneous ions that affect the emission intensity of the desired element. Some of these procedures are the dilution, radiation buffer, internal standard, the desired line-background correction, and addition methods.

This investigation demonstrated that many factors affect the emission intensity of potassium; some enhance, others depress, and to different extents, there may also be a compensation of interfering effects. Thus, in the flame analysis of potassium in a complex mixture such as fertilizers containing many different substances, it becomes difficult to correct for all of the interferences. The addition of large amounts of radiation buffers corrects some of the effects but also results in poorer atomizer performance.

In an attempt to obtain the most accurate and precise results for potassium, advantages are gained by careful clean-up of the sample solution into a simple system, preferably one cation and one anion. Afterward this unknown solution is atomized into the flame and the emission intensity of the desired element is compared with standards prepared from reagent grade potassium nitrate. In this way, both the sample and standard solutions are single systems of similar composition. It was felt that the application of the principles of ion exchange, plus chemical pretreatment, had considerable merit and would result in better flame analyses. Of course, good resolution or spread of wave lengths is also essential for high sensitivity, and the greater the dispersion achieved by the monochromator, the greater the signal to background ratio. Anion exchange resins were used to convert the anions in sample aliquot to nitrate, the unknown solutions were then compared with potassium nitrate standards. The ion exchange cleanup of the sample solutions allows one to obviate the addition of radiation buffers this results in improved atomizer performance and less background.

The following procedure can be used to further reduce the salt content of the aspirating solution by eliminating the ammonium nitrate, although it was found that ammonium nitrate did not affect the emission intensity of potassium at levels as high as 2000 p.p.m. of nitrate: Pass the sample aliquot through a column of a strongly basic anion exchange resin in the hydroxyl form. This converts all of the ammonium ions to ammonium hydroxide and potassium to potassium hydroxide. Remove the ammonium hydroxide by evaporation. Neutralize the potassium hydroxide with a few drops of hydrochloric or nitric acid. Make to volume and compare with known standards of potassium chloride or nitrate.

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