THE EFFECT OF VARYING THE CONCENTRATION OF CALCIUM AND POTASSIUM ON THE LINE INTENSITY OF PHOSPHORUS IN SPECTRO-ANALYSIS

by

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INTRODUCTION

Various errors that have been encountered in analytical spectro-chemistry have been discussed by several authors (15, 10). However by using the best technique, most of these errors may be reduced to a level comparable with or superior to the chemical wet methods for determinations involving lower concentrations of the elements investigated.

In the statistical study of the correlation between the concentration of the minor elements in plants and the metabolism and growth of these plants, the rapidity of the standardized spectrochemical determination far outweighs the inconvenience of setting up these standards. Although phosphorus in plants slightly exceeds the optimum percentage for most accurate spectrographic determination, sufficient accuracy can be obtained through special spectrographic technique. It was thought desirable, therefore, to develop an accurate procedure for the determination of phosphorus in concentrations encountered in plant ash, giving special attention to the effect on the accuracy of varying amounts of calcium and potassium also present in the plant.

Smith (17) has stated that the presence of constituents other than the one under investigation has no effect on the line intensity due to the latter constituent. That this is not true, especially for larger quantities of the extraneous elements (greater than one per cent), has been demonstrated by several investigators (1, 2, 3, 4, 5, 8, 20). It was con-

sidered, therefore, quite likely that the concentration of calcium and potassium found in plants would cause considerable effect on the line intensity of phosphorus. This investigation attempted to disclose the presence and extent of the effect of these extraneous elements, and to obtain data upon which a method to correct such errors could be based.

SURVEY OF LITERATURE

Twyman and Hitchen (19) through a study of the influence of copper and iron on the line intensities of cobalt and nickel, have suggested a direct examination of the unknown material to obtain a first approximation of the concentrations of the constituents. Using this approximation, they obtained a set of working curves which showed the influence of the variation of one of the constituents present on the line intensities of the other.

Another method of overcoming the effects of extraneous elements was used by Duffendack, Wiley and Owens (8) through their discovery that the influence of the extraneous element on the ratios of the intensities of the test element to the internal standard reached a maximum value. They added to their standard solutions and unknown a sufficient amount of the extraneous element to reach this maximum.

A systematized approach to the effect of one element on the line intensities of another has been made by other workers, who have attempted to establish (5) an ordered arrangement of the elements such that those elements above a certain element

will repress its line intensity, and those below will enhance it. Complicating factors prevent this series from being as successful as its electromotive counterpart. One such factor is the variation in the arc and spark conditions maintained by various observers, especially if the lines chosen differ markedly in energy requirements. Brode and Appleton (2) have demonstrated that the extraneous element may affect certain pairs of the probe and internal control lines, and not affect others. Any attempt, therefore, to obtain a reproducible series of the elements would necessitate a strict definition of the excitation conditions of the arc, and the excitation requirements of the lines of those elements.

The effect of extraneous anions on line intensities has been studied by Brode and Hodge (4), and by Brode and Brounique (3). They have concluded that, in a series of compounds of common cations and various anions, the line intensity of the cation was more sensitive for the lower boiling point compounds. Duffendack, Wiley, and Owens (8) suggest that all salts should be converted to a single acid radical, preferably one producing a low boiling point compound.

Still another method of overcoming the effects of extraneous elements is the use of a spectroscopic buffer. Hess, Owens, and Reinhardt (11) described this buffer as the added amount of a suitable salt which eliminated the effects of extraneous elements upon the analysis, and permitted the use of the same analytical curves for samples which differ in composition. A spectroscopic buffer must not be one of the test elements, and

should have a low excitation potential. Other considerations, which will be discussed later, are necessary in making a proper choice.

In reviewing the various publications on the effects of extraneous elements, it would seem that these effects are limited to certain concentrations, on either side of which the effects are nearly constant (8, 14, 20). Furthermore, the effects produced may be either positive or negative in their influence on the intensity of the line of the test element. The methods suggested to overcome errors due to these effects have been applied to this special problem to establish a suitable procedure for the accurate analysis of phosphorus.

EXPERIMENTAL PROCEDURE

Description of Apparatus

A large quartz spectrograph of the Littrow type, as shown in Plate I, was employed in this investigation. It is provided with interchangeable optical systems. One system uses glass of refractive index 1.625; the other system uses quartz optics. The quartz system was used in this research in order to include the spectral region of the phosphorus line investigated. The prism has a height of 57 mm, and a refracting face of 95 mm, which uses the full aperature of the lens. The lens is 70 mm in diameter and has a focal length of 1827 mm. This length of refracting face is maintained constant for full resolving power by stopping down the aperature in the vertical dimension only.

EXPLANATION OF PLATE I

A large quartz spectrograph of the Littrow type manufactured by the Bausch and Lomb Optical Company.

PLATE I

Full aperature was maintained throughout this research.

The spectrum produced by the quartz optics, 2100 to 8000 A.U., covers three ten-inch plates; however, the adjustments are so arranged that seven other positions are also available. To change from one region to another necessitates the rotation of the prism, movement of the prism and lens to a new focus, and a change in the tilt of the plate. The first two adjustments are co-ordinated by means of a cam, which causes the prism to rotate as it is moved forward or back in focusing.

The dispersion of this instrument for the quartz optics is 2.7 A.U. per mm at 2535 A. U. This is sufficiently high to separate the phosphorus line from those of interfering elements. The slit is bi-lateral, and is protected in front from external injury by a quartz plate.

Data obtained by use of the step sector disc made possible the plotting of the characteristic density versus log exposure curve of the photographic plate at the wave length of the phosphorus line. The step sector was placed between the light source and the slit and adjacent to the latter. The angular lengths vary from one step to the next longer one in the constant ratio of 1 to 1.5.

Interchangeable with this disc is an adjustable sector on the motor mount. This sector was used to adjust the light exposure for the various concentrations of the phosphorus. The disc is adjustable from zero to 180 degrees opening with graduations indicating fractional openings. It is to be noted,

however, that the fractional opening corresponding to one is an actual opening of 180 degrees of a circle, and therefore allows only one-half of the incident light to pass through. To avoid confusion in this research, where a sector opening is referred to, the fractional openings indicated on the disc have been divided by two in order to indicate the actual fraction of the incident light which passed through the sector.

The optical density of the lines were measured by an Allied Research Laboratories-Dietert densitometer of the projection type (4), as shown in Plate II. In this densitometer, a slit, 0.012 by 1.1 mm, is placed on the emulsion side of the plate and moved over the spectral line by means of a motor driven scanning carriage. A projection lamp supplied with a 6 volt, 60 cycle voltage regulated input produces constant illumination, which is focused by a lens through the slit and plate to a vacuum photo-cell. The current produced is amplified by a bridge circuit to actuate a galvanometer. A section of the plate is projected simultaneously on the screen. In operation, the scanning mechanism was rotated until the slit was perfectly aligned with the spectral line. Then the plate was moved until a clear portion was projected between the dots marked on the screen. The scanning handle was then pushed and the meter adjusted to 100. The line was scanned in a similar manner, and the minimum reading gave the per cent transmission. The galvanometer reading was corrected by means of the calibration curve described in a later part of this paper. Check

EXPLANATION OF PLATE II

Allied Research Laboratories-Dietert densitometer of the projection type.

PLATE II

readings gave results which agreed within a fraction of a per cent transmission.

The source of excitation was a direct current generator maintained at a potential of 120 volts. A ballast resistor was placed in series with the generator to maintain a steady current of about eight amperes.

Choice of Phosphorus Line

The line of the phosphorus spectrum corresponding to a wave length of 2535.7 A.U. has been reported (6) sensitive to 0.005 milligram of phosphorus on the electrode, and is relatively free of interfering lines of other elements. In order to place this line near the center of the plate, position 7 was chosen. This position had been recently checked on the Littrow by exposing iron spectra at various foci, holding the tilt constant; then at various tilts holding the focus constant. The corrected position was at a focus setting of 154, and a tilt of 204. Table 1 lists the phosphorus line together with lines of the interfering elements. It is to be noted that although there is very little separation in certain of the wave lengths, the instrument used gives sufficient dispersion to permit good separation of these lines. The only one which might interfere is the iron line at 2535.7, but the alternate phosphorus line at 2534.0 might be calibrated for samples containing a considerable amount of iron. None of these interfering elements caused difficulty in this research, and the internal standard element (cobalt), which was finally chosen, had a

line easily separated by the spectrograph.

Table 1. Lines of elements that interfere with phosphorus line of wave length 2535.7 A.U.

Element	Line (A.U.)	Separation
phosphorus	2535.7	
silver	2535.3	0.4
cobalt	2533.8	1.9
iron	2535.6	0.1
mercury	2536.5	0.8
manganese	2533.1	2.6
titanium	2535.9	0.2
platinum	2536.4	0.7
nickel	2536.0	0.3
tantalum	2536.6	0.9

Preparation of Electrodes

The standard commercial electrodes supplied by the National Carbon Company were found to be free of all pertinent elements, and were used throughout this research. The 5/16 inch carbons were cut into one inch lengths. The ends of the anodes were shaped like a crater, 1.5 mm deep (Fig. 2). The ends of the cathodes were shaped like a bullet, on the end of which extended a cylindrically shaped projection about 1 mm in diameter, and 3 mm in length (Fig. 1). This latter projection was found useful in preventing wandering of the arc, and in

Fig. 1. Cathode

Fig. 2. Anode

penetrating the hard crust of the dried sample to enable striking an arc.

The crater of the anode was filled with a saturated solution of carnauba wax in carbon tetrachloride and dried in an air oven for 15 minutes at 100 degrees Centigrade.

Introduction of Sample on Electrodes

To increase precision, three electrodes were run for each solution, and this number was increased at doubtful points. A 0.1 ml volume of the sample was introduced on the cooled electrodes by means of the AML pipette, shown in Plate III. The diameter of the orifice was varied until four drops were required to give this volume. The volume of this sample was determined by weight until it was definitely established that four drops gave a volume of 0.1 ml, with a variation of less than one per cent.

The electrodes were again placed in the air oven and dried for thirty minutes at 80 degrees Centigrade; then the temperature was maintained at 100 degrees Centigrade for a minimum period of four hours.

Preparation of Phosphorus Standard

While any range of phosphorus concentrations could have been used for this study, it was considered sufficient to include those concentrations encountered in spectrographic studies of plants. These concentrations conformed to the

EXPLANATION OF PLATE III

Allied Research Laboratories pipette.

PLATE III

standard solutions made up by the Federal Soft Wheat Laboratory (13), which included concentrations of the element found in flours, bran, wheat and grasses. That laboratory used potassium dihydrogen phosphate to prepare the standard solution for the elements potassium and phosphorus, but in this research it was necessary to use meta phosphoric acid to prepare the phosphorus standard. A standard solution of 6.45 grams of meta phosphoric acid per liter was prepared, corresponding to 2.5 milligrams of the elemental phosphorus per milliliter. For a preliminary study of the phosphorus line density, the dilutions given in Table 2 were used.

Table 2. Working concentrations of phosphorus as used in the preliminary tests.

Sample	Phosphorus standard	Water	Phosphorus on electrode
1	1.0 milliliter	3 ml	0.03 milligram
2	1.5	2.5	0.09
3	3.0	1.0	0.18

Determination of Exposure

To determine the effect of one extraneous element on the phosphorus line only, Gerlach's internal standard method (9) had to be temporarily abandoned in favor of Slavin's total energy method (16). In this method, the light energy is integrated by the photographic plate over limits which are

certain to include the total vaporization of the test element.

Sample 3 from Table 2 was introduced on the electrodes, prepared as described, and completely vaporized in the arc while moving the plate at five second intervals. The ARL densitometer was used on the 2535.7 A.U. line produced, and a clear plate reading was obtained at the fourth spectrum, corresponding to a cumulative exposure of fifteen seconds. Due to the inertia of the emulsion of the plate, however, it was estimated that complete volatilization of the largest sample of phosphorus took place in twenty seconds.

To allow for delay in volatilization of phosphorus resulting from the presence of the extraneous elements, sixty seconds was taken as a standard volatilization period. Variations in exposure were produced by means of the variable rotating sector. These variations, together with the variations in the concentration of the phosphorus, are listed in Table 3.

From the calibration of the plate, which follows in the next section, the optimum density of the phosphorus line was found to be about 1.0 when the addition of an extraneous element decreased the density of that line. Therefore the indicated sector to produce this density with a 60 second exposure is seen to be sector 1 for 0.03 milligram of phosphorus on the electrode; sector ½ for 0.09 milligram; and sector 5/16 for 0.18 milligram.

In addition to exposure conditions, the spectral purity of the meta phosphoric acid was ascertained by this plate.

Table 3. Determination of exposure of standard phosphorus samples.

Milligram phosphorus on electrode	Sector	Line density of 2535.7 A.U.
0.03	1	1.00
0.03	½	0.52
0.03	¼	0.29
0.09	1	1.40
0.09	½	1.00
0.09	¼	0.54
0.18	1	1.48
0.18	½	1.10
0.18	¼	0.60

Calibration of Plate

It was desired in this research to determine the effect on the line intensity of phosphorus by the addition of extraneous elements. This intensity was integrated over a 60 second exposure and measured by the blackening effect produced on an Eastman 33 photographic plate. This blackening was quantitatively measured as optical density by an ARL densitometer, and found to be proportional to the log of the intensity within a considerable range of intensities. As long as the conditions of exposure were limited to those which produced a density on this straight line portion, a change in the intensity of the light was accurately measured by a change in the optical density

produced.

In this research, however, it was discovered that even starting with the greatest density on the straight line portion, the extraneous elements repressed the intensity of the phosphorus line to the toe of the D/log E curve. To obtain an accurate measure of the repression of the intensity in higher concentrations, it was necessary to correct the densities of these lines by means of a D/log E curve obtained from known relative intensities of light. These relative intensities were obtained as previously described by means of a rotating step sector in front of the slit of the spectrograph. This sector, as well as the variable sector, was rotated well above the minimum interruptions per second specified by Webb (21).

Eastman 33 plates were exposed to an iron spectrum in position seven. After exposure they were developed for five minutes in Eastman Xray developer (dil. 1:2) at a temperature of 68 degrees Fahrenheit. They were then washed for 15 seconds and fixed for 10 minutes in Eastman Acid Hypo at the same temperature. After fixing, the plates were washed for one-half hour, squeegeed, and carefully dried in a dust free current of air. This photographic process was carefully duplicated for every plate exposed during this research.

The densities of the lines of various step exposures in the region of 2535 A.U. were determined by means of the ANL-Dietert densitometer. This region in which the phosphorus line was located was chosen because of the variation of the plate

gamma with the wavelength (14). These densities were plotted against the log of the relative step sector openings as shown in Fig. 3. Several lines were used in this region to check the slope, and to cover a greater range of exposures.

Two methods of applying the calibration curve to data were used. One method used the calibration curve in Fig. 3 directly. The galvanometer readings of the ANL densitometer were converted to density values, and accepted as correct for the range 0.45 to 1.3. For density values below 0.45, the ordinate corresponding to this value on the curved toe was replaced by the corrected ordinate on the straight dotted line.

Another method found to be more convenient in certain cases corrected the galvanometer readings directly by using Fig. 4. This graph was obtained by plotting the observed galvanometer readings against the corrected value that would make the D/log E curve linear. All values of the galvanometer readings below 30 were found to be correct, except for extremely dense lines, which were avoided during this research.

It is to be noted from Fig. 3 that relatively high densities are linear for the Eastman 33 plates, but the galvanometer readings were not as accurate for the heavier lines. As a compromise for these inaccuracies, and as a convenience in avoiding background correction, the density of the heaviest line was adjusted to 1.0. Background errors are reported (14) not great if the line densities are high, and background density is low. There was practically no background emission in the region of the 2535.7 A.U. line, and all plates showing fog

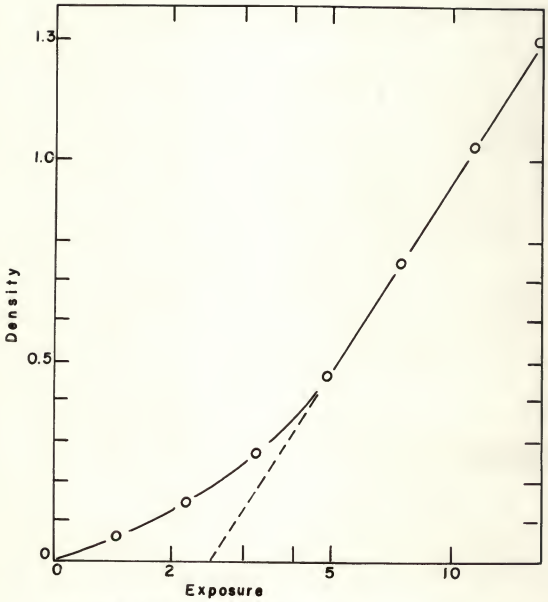

Fig. 3. Eastman 33 calibration curve.

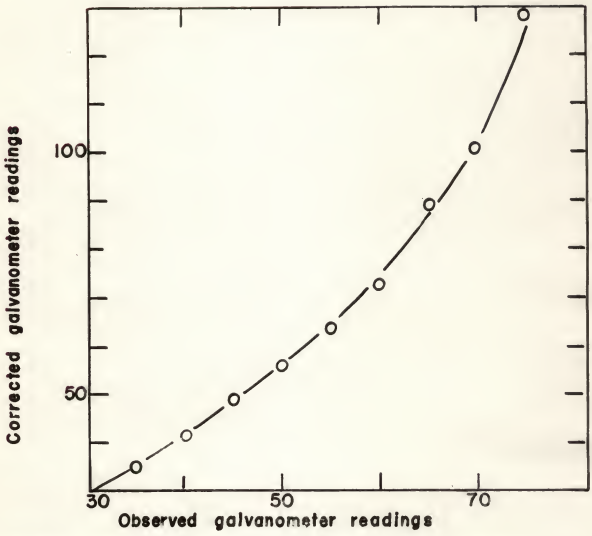

Fig. 4. Correction from density readings to intensity values.

were discarded.

Effect of Potassium on Intensity of Phosphorus Line

In the determination of the effect of the extraneous elements, potassium and calcium, on the line intensity of phosphorus, two results were desired. In one it was desired to determine and correct the effect of the extraneous elements in the concentrations found in materials to be analyzed. On a more theoretical basis it was also desired to determine and correct, if possible, the effects of these extraneous elements in concentrations far beyond those occuring in any materials for which the concentration of phosphorus was to be determined. Therefore, a range of from 0.025 to 2.5 milligrams of potassium on the electrode was obtained by preparing one potassium standard containing 100 grams of potassium per liter, and another by diluting this standard 1 to 10. The standards contained 21.025 and 210.25 grams of potassium chloride per liter of solution. These potassium solutions were added to the various phosphorus solutions according to Table 4. Sufficient water was added to each solution to give a total volume of four milliliters, as before. A 0.1 milliliter of each sample was added to the prepared electrodes, and the regular spectrographic, photographic and densitometeric procedure was followed. A photographic positive enlargement of the significant region of the phosphorus line is shown in Plate IV. All of the lighter lines were corrected to linearity, and the three

EXPLANATION OF PLATE IV

The twelve spectrograms shown in this plate were produced from a constant 0.03 milligram sample of phosphorus on the electrode, with the increasing quantities of potassium as follows: Spectrograms 1-3, 0 micrograms of potassium; spectrograms 4-6, 125 micrograms of potassium; spectrograms 7-9, 251 micrograms of potassium; and spectrograms 10-12, 503 micrograms of potassium. The resulting repressing effect on the phosphorus line of wave length, 2535.7 A.U., is shown by the diminishing of the intensity of this line at position 100.9.

PLATE IV

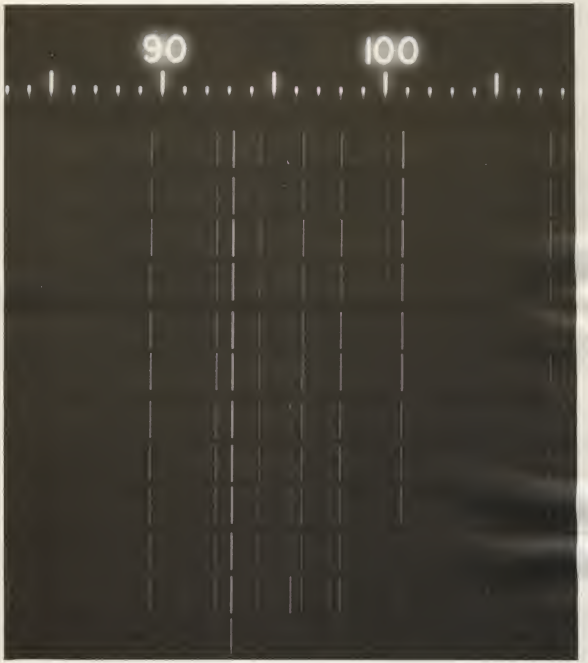

Table 4. Various quantities of potassium added to phosphorus solutions.

Sample	Potassium standard	Micrograms K on electrode	Log micrograms potassium
1	0.10 ml dil.	25	1.4
2	0.25 "	62.5	1.8
3	0.50 "	125.0	2.1
4	0.75 "	187.5	2.3
5	1.00 "	250.0	2.4
6	1.00 ml con.	2500.0	3.4

duplicate samples were averaged for each concentration, except for discarding an occasional sample that was known to be in error. This reduced the probable error to a smaller value than that reported in another part of this paper. The variation in the density of the phosphorus line with increasing amounts of potassium is shown graphically in Fig. 5. As would be expected, a given small amount of potassium has the greatest effect on the 0.03 milligram sample of phosphorus, but the higher concentrations of potassium produce a common maximum effect on all three concentrations of phosphorus.

Selection of Internal Control

Slavin's total energy method (16) was used in the spectrographic analysis of phosphorus, and it was found that the presence of potassium had a marked effect on the line intensity of phosphorus, independent of any variation in spectrographic

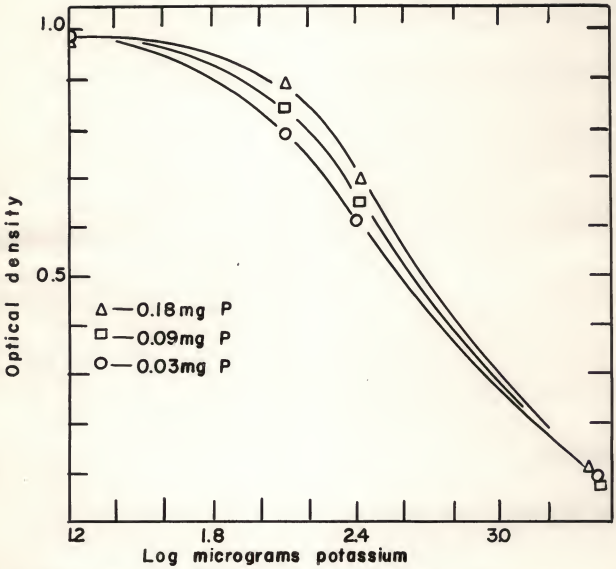

Fig. 5. Effect of potassium on line intensity of phosphorus.

or photographic procedure. Slavin considered only mass and differential volatilization as determining the repressing effect of an easily vaporized extraneous element. The enhancement of the test element by certain extraneous elements was not explained. Other workers (9, 12) have considered relative excitation potentials of the elements as influencing the intensity of the test element at the time it is excited in the arc. Langstroth and McRae (12) state that not only must the mechanism responsible for the release of material from the electrode be considered (as does the total energy method), but also the behavior of the material along the inter-electrode distance. This behavior, which he explains as the transport phenomena in the arc and spark, may be described as a variation in the intensity of an excited atom with the location of that atom relative to the inter-electrode axis. The relative distribution of this intensity depends not only on the ionization potentials and masses of each element, but also on the ionization potentials of other atoms present between the electrodes. If the atoms of the extraneous element are more easily ionized than the test element, the intensity distribution of the test element falls off more sharply toward the unloaded electrode than it does when the easily ionized atoms are absent. Since only a section of the distance between electrodes is focused on the slit, both enhancement and repression of line intensity is accounted for by this shift in distribution in the presence of extraneous elements. This work indicated the

necessity for the use of a spectroscopic buffer, and provided certain qualifications for that buffer and of the internal standard element.

Using the total energy method, it was desirable but not essential that the internal standard have the same boiling point as the phosphorus. Considering the transport phenomena (16), however, it was desirable also that they have as nearly as possible the same ionization potential. In addition, it was desirable to have an internal standard having nearly the same mass as phosphorus.

Separate from the transport phenomena, it was desirable to choose a line close to, but not interfering with, the phosphorus line. Furthermore, the excitation potentials of the phosphorus and the internal standard lines should be as nearly equal as possible. Table 5 lists the internal standards tested, and their respective masses and ionization potentials.

Table 5. Possible internal standards for phosphorus.

Element	Ionization potentials	Atomic weight	Wavelength A.U.	Relative intensity
Phosphorus	11.0	31.0	2535.7	100
Arsenic	10.5	74.9	2456.5	100
Cobalt	8.5	58.9	2544	40
Tin	7.5	118.7	2546	100

The ionization potential of arsenic is favorable, and the mass ratio is not too high; however, the only line of comparable intensity with the phosphorus line lies too far from it on the plate. Upon exposing a plate it was discovered that even this line was too faint at the exposure conditions required for the phosphorus determination.

The tin was chosen as a possible internal standard in spite of its undesirable characteristics, because it had been reported (18) as a suitable simultaneous standard for boron, manganese and magnesium. The spectroscopic buffer used in this work undoubtedly compensated for some of the undesirable behavior of the line, as shown in Fig. 6. This behavior was to be expected from the high mass ratio as compared with phosphorus, and also its low ionization potential.

Cobalt presented a more favorable mass ratio, and a higher ionization potential. Furthermore, exposure conditions corresponding to that for phosphorus, produced a line of comparable density and excitation potential.

Using 0.2 milligram of cobalt on the electrode, a line whose density was 0.5 was produced using a 60 second exposure at ½ sector opening. Varying quantities of potassium were added to this constant quantity of cobalt, and, following the standard procedure, the effect of the potassium on the line intensity of cobalt was obtained as shown in Fig. 7. It is thus noted that potassium produces a repression on the line intensity of cobalt, quantitatively similar to its repressing

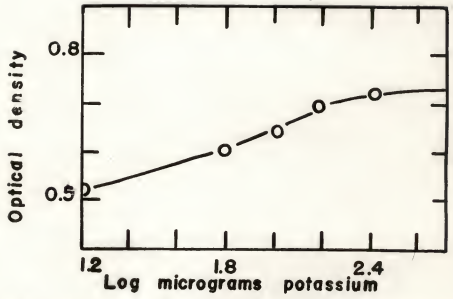

Fig. 6. Effect of potassium on line intensity of tin.

effect on phosphorus. The cobalt, therefore, should make a suitable internal standard for phosphorus, provided that variations in the concentration of phosphorus do not cause too great a variation in the intensity of the cobalt line.

This latter effect was determined by using a constant 0.2 milligram sample of cobalt on the electrode, and varying the amount of phosphorus. The effect produced is shown in Fig. 8. It is seen that, while an enhancing effect is produced, the effect is nearly constant for all concentrations of phosphorus.

Varying quantities of potassium were added to a constant quantity of 0.1 milligram of cobalt and 0.03 milligram of phosphorus on the electrode, The densities of the cobalt and phosphorus lines as well as their ratios were plotted against varying quantities of potassium added, as shown in Fig. 9. It is seen that the internal standard procedure greatly improves the constancy of the phosphorus line, but a considerable repression is still encountered. A much greater improvement was obtained by the subsequent use of a buffer described later in this paper.

Effect of Calcium on Intensity of Phosphorus Line

Following a procedure similar to the one described for using potassium as the extraneous element, two standard calcium solutions were prepared. One contained 5 milligrams of calcium per milliliter (13.85 grams calcium chloride per liter), and the other contained 0.5 milligram of calcium per milliliter, obtained by diluting the first solution 1 to 10. These calcium solutions

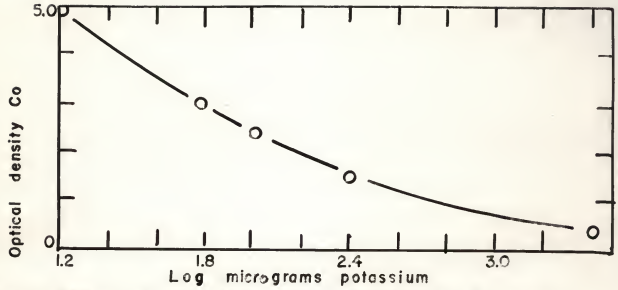

Fig. 7. Effect of potassium on line intensity of cobalt.

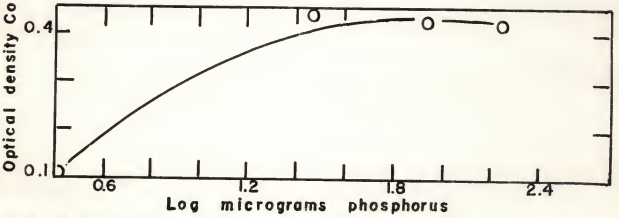

Fig. 8. Effect of phosphorus on line intensity of cobalt.

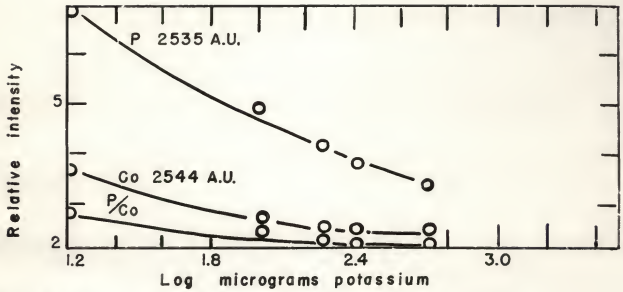

Fig. 9. Effect of potassium on line intensity ratios.

were added to the phosphorus standards according to Table 6. Sufficient water was added to each solution to give a total volume of 4 milliliters, and a 0.1 milliliter of each sample was added to the prepared electrodes.

Table 6. Various quantities of calcium added to phosphorus solutions.

Sample	Calcium standard	Micrograms calcium on electrode	Log micrograms potassium
1	0.25 ml dil.	3.1	0.49
2	0.50 "	6.2	0.79
3	1.00 "	12.5	1.10
4	1.00 ml con.	125.0	2.10

The variation in the density of the phosphorus line with increasing amounts of calcium is shown in Fig. 10. The effect of the calcium on the phosphorus is seen to be very slight, especially in those concentrations ordinarily found in plant material. However since cobalt is proposed as a suitable internal standard for phosphorus, it was desirable to determine the effect of calcium on the line intensity of cobalt.

Using a constant 0.1 milligram quantity of cobalt on the electrode, the calcium content was varied, and the electrodes arced 60 seconds at a 3/16 sector opening. Figure 11 gives the resulting effect produced by the calcium on the cobalt line. It is seen that the calcium produces an enhancing effect on the cobalt line. In the absence of a buffer, therefore, undesirable ratios of the cobalt to the phosphorus lines could be

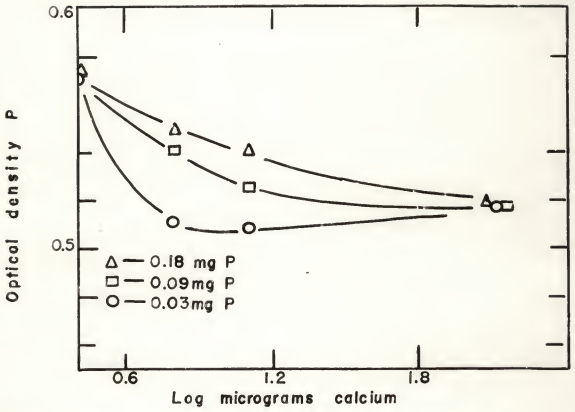

Fig. 10. Effect of calcium on line intensity of phosphorus.

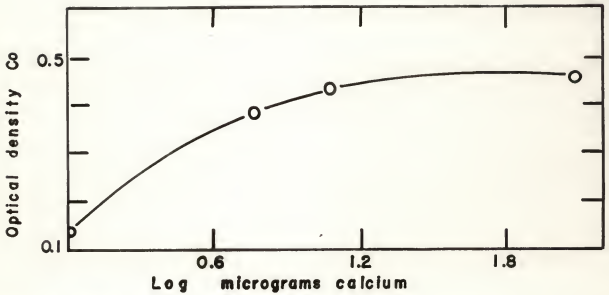

Fig. 11. Effect of calcium on line intensity of cobalt.

expected as the quantity of calcium increased.

To determine the extent of this effect, a constant quantity of 0.1 milligram of cobalt and 0.03 milligram of phosphorus was placed on each electrode, together with varying amounts of calcium. The results of this investigation are shown in Fig. 12, and indicate a greater need for a suitable buffer with calcium as the extraneous element, than when potassium alone is present.

Selection of Spectroscopic Buffer

In seeking a suitable spectroscopic buffer, some of the suggestions of Langstroth and McRae (12) were found helpful. Considering the transport phenomena in the arc, they suggested an element of low ionization potential. Such elements so greatly alter the transport phenomena that reasonable variations in the extraneous element composition should not appreciably affect it. Lithium chloride had been used previously in this laboratory with reported (18) success, but its use in connection with the present problem met with inconsistent results. This was attributed to the flaking off during the arcing process. Similar results were obtained from the carbonate of lithium.

Following the principles suggest by Langstroth and McRae (12), the carbonate was converted to the tartrate by the addition of tartaric acid. It was confirmed that the organic salts form a more suitable layer on the electrode, and did not flake off during the arcing process.

Eighty seven grams of lithium carbonate was added to 198 grams of tartaric acid to produce 213 grams of lithium tartrate.

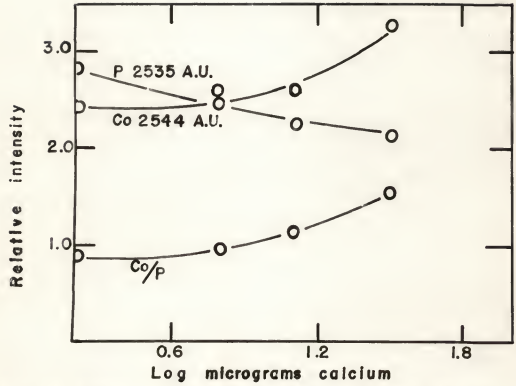

Fig. 12. Effect of calcium on line intensity ratios.

This quantity required one and one-half liters of water to dissolve it, producing a concentration of 142 milligrams of lithium tartrate per milliliter. One milliliter of the buffer solution was added to make up the 4 milliliter sample for a repetition of each previous test. The preparation of all solutions were duplicated with one exception. It was found that one milliliter of the concentrated calcium chloride solution produced a precipitate with the lithium tartrate, making the pipetting of the 0.1 milliliter sample impossible. A 10 milliliter sample of the lithium tartrate solution was titrated with the dilute calcium chloride solution, and it was found that 22.5 milliliters were required to produce a precipitate. Therefore, the maximum calcium concentration used in the presence of the buffer was 2.25 milliliters of the dilute calcium chloride solution.

The success of the buffer chosen is best shown by the graphs obtained from their use. A leveling off is produced without exception, but to a lesser degree in certain cases.

Figure 13 shows a complete nullification of the repressing effect of potassium on the phosphorus line. A certain degree of repression exists after the use of the buffer in the case of cobalt, as shown in Fig. 14. However, Fig. 15 reveals the lack of a corresponding repression in the presence of the phosphorus, and a nearly constant ratio of the intensities of the cobalt to the phosphorus line is retained throughout increasing quantities of potassium.

A similar improvement in the repression of the phosphorus

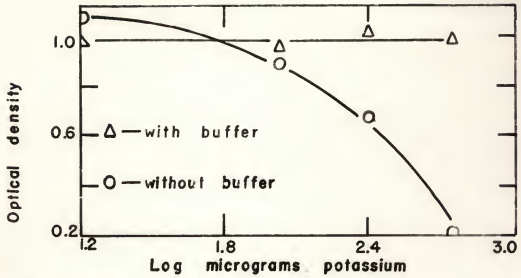

Fig. 13. Buffer action on K repression of P line intensity.

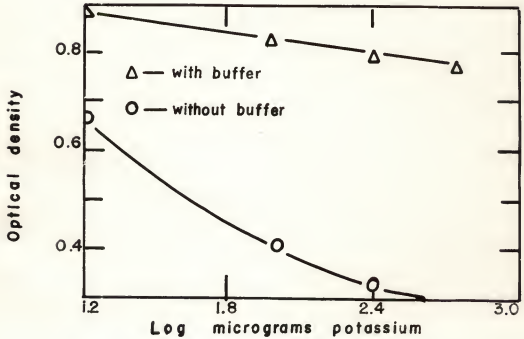

Fig. 14. Buffer action on K repression of Co line intensity.

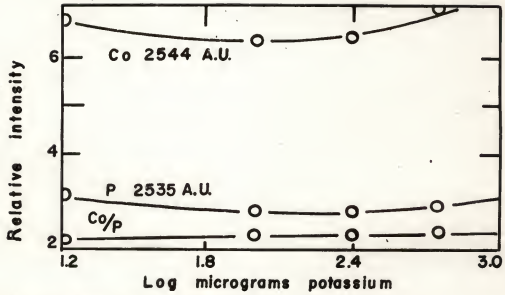

Fig. 15. Effect of potassium on line intensity ratios, with buffer.

line by the addition of calcium is observed in Fig. 16. The enhancement of the cobalt line is maintained at a constant intensity, as seen in Fig. 17. Figure 18 shows the constant ratio of the intensities of the cobalt to the phosphorus line with the varying quantities of calcium added.

Precision of Method

In some of the graphs showing the effects of the extraneous elements on the line intensity of phosphorus, the curve was not only non-linear, but at low concentrations a minimum repression was evident. Although this effect has been reported (5) from a theoretical and experimental basis, it was desired to ascertain whether this behavior was due to experimental error, or to a combination of independent factors. A series of forty electrodes containing the same amount of phosphorus was given identical exposures. The density of the phosphorus line produced was determined as before, and tabulated as shown in Table 7. It is seen that the standard deviation from a mean density of 0.358 is 0.028, giving a standard error of 0.004 for the mean density of the 40 electrodes.

It is more significant to determine the standard error for the three duplications actually run; namely, 0.016 for the mean density of 3 electrodes. If a point deviated from the smooth curve outside the limits of this standard error, more than three samples were arced to increase the reliability of that point.

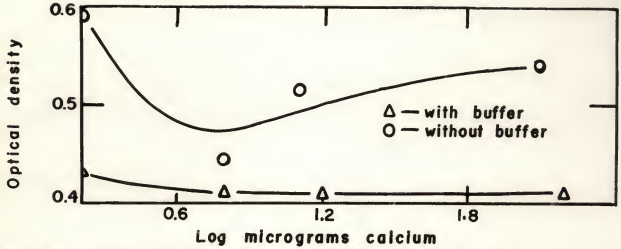

Fig. 16. Buffer action on Ca repression of P line intensity.

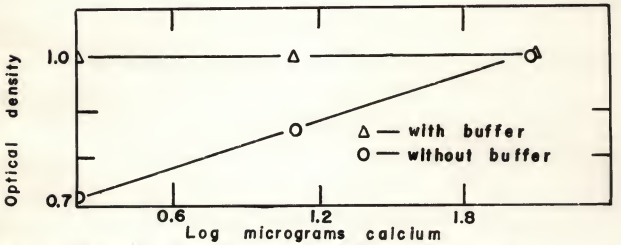

Fig. 17. Buffer action on Ca enhancement of Co line intensity.

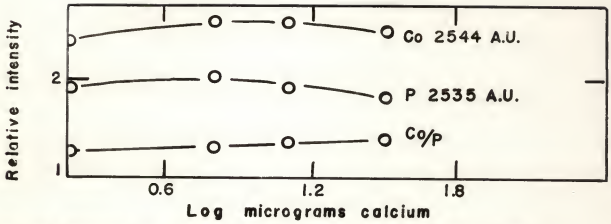

Fig. 18. Effect of calcium on line intensity ratios, with buffer.

Table 7. Precision of determination of the line intensity of 0.05 milligram phosphorus sample.

Density	x	$x^2 \cdot (10^{-5})$	Density	x	$x^2 \cdot (10^{-5})$
0.397	0.039	152	0.398	0.040	160
0.347	0.011	12	0.347	0.011	12
0.367	0.009	8	0.367	0.009	8
0.398	0.040	160	0.397	0.039	142
0.398	0.040	160	0.338	0.020	40
0.398	0.040	160	0.357	0.001	0
0.337	0.021	44	0.367	0.009	8
0.337	0.021	44	0.337	0.021	44
0.398	0.040	160	0.328	0.030	90
0.337	0.021	44	0.367	0.009	8
0.347	0.011	12	0.367	0.009	8
0.367	0.009	8	0.328	0.030	90
0.398	0.040	160	0.357	0.001	0
0.357	0.001	0	0.432	0.074	547
0.337	0.021	44	0.398	0.040	160
0.387	0.029	84	0.398	0.040	160
0.377	0.019	36	0.387	0.029	84
0.347	0.011	12	0.347	0.011	12
0.337	0.021	44	0.319	0.039	152
0.337	0.021	44	0.347	0.011	12

Mean density = $\Sigma D/N = 14.325/40 = 0.35$

Standard deviation = $s = \sqrt{\Sigma x^2/N} = \sqrt{3125 \cdot 10^{-5}/40} = 0.028$

CONCLUSION

A marked repression, which is non-linear, of the line intensity of phosphorus was produced by increasing quantities of potassium. A very slight repression of the line intensity of phosphorus was produced by increasing quantities of calcium. This repression was obtained in spite of the use of Slavin's total energy method.

The best correction of the error due to these extraneous elements was obtained through the consideration of the transport phenomena in the arc to develop a suitable internal standard, and spectroscopic buffer.

It was discovered that, while cobalt was the best available internal standard, only fair results on the constancy of the line intensity ratios were obtained with increasing quantities of the extraneous elements, potassium and calcium. However, upon the addition of a suitable spectroscopic buffer, lithium tartrate, constant ratios were obtained.

It can therefore be concluded that an accurate working curve for the determination of phosphorus in a sample can be obtained in the presence of large variations in the quantity of potassium and calcium through the use of cobalt as the internal standard, and of lithium tartrate as the spectroscopic buffer.

ACKNOWLEDGMENT

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