

FLAME PHOTOMETRIC ANALYSIS OF COPPER
WITH ION EXCHANGE SEPARATION OF INTERFERING IONS

by

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INTRODUCTION

During the past few years increasing emphasis has been directed toward the application of flame spectrophotometric methods of analysis. As a rule, flame photometric analysis is more rapid and simpler than conventional volumetric, gravimetric, and colorimetric methods of quantitative analysis. It would seem desirable for this reason to improve flame photometric techniques for the determination of as many elements as possible. Many elements have been studied extensively and acceptable methods of analysis have been proposed for some, notably the alkali and certain alkaline earth metals (2, 3, 5, 10). Flame photometry is similar to spectrographic arc and spark analysis in that the spectral emissions of certain elements are enhanced or suppressed by the presence of certain other elements (4, 13, 20, 22). This effect makes it necessary in many cases to either compensate for the interferences by some means or remove the substances causing the interferences.

The flame photometric analysis of copper has been studied and reported by several investigators (6, 7, 9, 11, 16, 17). It is generally believed that various cations and anions in solution affect the net emission of copper. Several methods of eliminating the interferences have been proposed. Some authors suggest methods of correcting for changes in background radiation (6, 16). The use of an internal standard has been reported (6). Methods for the separation or extraction of copper from various solutions have been proposed (7, 9, 11, 17). The use of ion exchange resins has been reported as a means of removing interfering anions from solutions to be analyzed flame photometrically (1, 8). Kraus and Moore (12) reported a method of separating the divalent transition elements by means of an ion exchange column. Their work, however, was not done in connection with flame photometry.

The purpose of this investigation was to study the flame photometric analysis of microgram quantities of copper, specifically in mineral mixes. The investigation consisted of determining what effects other substances present in mineral mixes have on copper flame emission and then attempting to remove the interfering ions from solution through the use of ion exchange resins.

SURVEY OF LITERATURE

The first determinations of copper using the flame as an excitation source were modifications of the Lundegardh method (14, 15) of flame spectrographic analysis. Robinson, et al. (19) reported on the flame analysis of copper and about a dozen other elements in biological materials. Reproducible results within an accuracy of five per cent were reported. Human and cow's milk, blood, urine, feces, and tissue were some of the samples upon which analyses were carried out. Robinson, et al. (19) reported that differing concentrations of magnesium, iron, and aluminum caused widely varying background effects.

Gerber, et al. (9) determined iron, manganese, copper, and cobalt in mineralized salt using a flame photometer. The metals were separated from the salt solution by precipitating them as hydroxides with sodium hydroxide. The precipitated hydroxides were then dissolved in eight normal hydrochloric acid and the iron extracted with isopropyl ether. Determinations were then made for the various cations after proper dilutions. Gerber, et al. (9) stated that results for copper and cobalt were not so satisfactory as those usually demanded in analytical work.

Massey (17) reported a method for the flame photometric analysis of copper in plant material. Copper was extracted from a 0.1 normal hydrochloric acid solution of plant ash with a chloroform-kerosene solution of dithizone. The

copper determination was then made on this organic mixture. The chloroform-kerosene solvent enhanced the copper emission, thus making a more sensitive determination of very small amounts of copper. Massey (17) emphasized the necessity of preventing evaporation of the chloroform. Results were reported to compare reasonably with the official A.O.A.C. method.

A chloroform solution of salicylaldoxime was used to extract copper from aqueous solutions of ferrous alloy samples by Dean and Lady (7). Citrate was employed to buffer the solution at pH 3 and complex the iron, thereby preventing its coextraction. The organic extract was aspirated directly into the flame. The 324.7 millimicron copper line was used for the determinations. Changes in the flame background were corrected by taking readings of the samples at 325.0 millimicrons and subtracting these values from the copper emission readings.

Jordan (11) determined the copper content in gasolines by extracting the copper from the gasoline with four molar hydrochloric acid. This acid extract was used for the flame photometric analysis. To compensate for any effect of the hydrochloric acid on copper emission, the copper standard solutions also were made four molar with respect to hydrochloric acid. Jordan (11) reported reproducible results within ± 10 per cent accuracy for the solutions which ranged in concentration from one to five milligrams of copper per liter.

Waring (22) reported on the flame photometric determination of copper and several other elements in materials related to the aluminum industry. He pointed out that a knowledge of the various emission interferences is necessary before accurate determinations can be made for any particular element.

An extensive investigation was carried out on the interferences of numerous cations and anions on the spectral emission of copper in 80 per cent methanol solutions by Manna, et al. (18). They reported that hydrochloric and sulfuric

acids caused the spectral emission of copper to decrease as concentrations of the acids increased. Acetic acid caused copper emission to be increased. Nitric acid caused a slight enhancement at a concentration of two molar. Phosphoric acid concentrations up to 0.1 molar did not affect the net copper emission but caused an increase in background radiation. Two molar phosphoric acid exerted a pronounced inhibiting effect on the radiant power of copper. Iron, magnesium, calcium, and potassium were among the cations investigated which caused copper emission to be repressed. Manganese was reported to exert a slight enhancement. A procedure for correcting for the interferences of the cations studied was presented. The technique reported is somewhat the same as that proposed later by Dean and Lady (7).

Dean (6) reported that perchloric, hydrochloric, nitric, and sulfuric acids do not interfere with copper emission in aqueous solutions when present in concentrations of one molar or less. At higher concentration levels an increase in flame background results. Of the cations investigated, only cobalt and nickel were reported to interfere with the emission of copper. The use of silver as an internal standard was investigated. Although proving satisfactory the use of an internal standard did not significantly improve the results. Dean (6) concluded that the interferences present in the nonferrous alloys studied caused changes in flame background only and did not affect the net copper emission.

Sulfate and phosphate ions which repress the flame emission of such metals as calcium and magnesium have been successfully removed from solutions through the use of an anion exchange column (1). Results listed showed that an adequate removal of sulfate and phosphate ions was accomplished without any noticeable loss of the cation involved which was calcium.

The use of an ion exchange resin to remove undesirable anions also was reported by Gehrke, et al. (8). Their work involved the flame photometric

analysis for potassium in fertilizers. The resin and sample solution were shaken together in a flask and then the mixture was filtered to remove the resin. This technique proved more rapid than the use of a resin column and the results were quite acceptable.

Kraus and Moore (12) investigated the separation of the divalent transition elements, manganese to zinc, in hydrochloric acid using an anion exchange resin column. The separation is based on the fact that the negatively-charged chloride complexes of these transition elements vary widely in their adsorabilities on the column. By controlling the concentration of hydrochloric acid used as the eluting agent, Kraus and Moore (12) were able to achieve an apparently complete separation of the transition elements under investigation.

EXPERIMENTAL

Instruments Used

Emission measurements were made with a Beckman Model DU Spectrophotometer equipped with photomultiplier unit and a Model 9200 flame attachment. The instrument also was supplied with a 92300 Spectral Energy Recording Adapter and Brown Type 155 Recorder. A Model 4080 atomizer-burner using an oxygen-acetylene mixture was the excitation source. All instrument settings were kept the same throughout the work. The settings were as follows:

Oxygen pressure, lbs./sq. in.	10
Acetylene pressure, lbs./sq. in.	5
Sensitivity control	max.
Selector switch, position	0.1
Phototube resistor, megohms	22
Slit width, millimeters	0.03

Dean (6) reported that the 324.7 millimicron copper line is the most sensitive for concentrations of copper less than 100 micrograms per milliliter. Since the copper concentrations in this work were all below this level, the 324.7 millimicron line was selected. The Spectral Energy Recording Adapter and Brown Recorder were employed for all copper emission readings. The use of these attachments permits scanning the desired wave lengths of the spectrum. In this work the wave length range of from 324.0 to 326.0 millimicrons was scanned in order to record the emission of the 324.7 millimicron copper line and the flame background on both sides of the line. A Spectral Energy Recording Adapter scanning speed of 30 was selected for this investigation. A scanning speed of 30 indicates the time in minutes required to scan four-fifths of a single scroll revolution. The chart speed of the Brown recorder was set at four inches per minute. This scanning speed-chart speed combination gave a satisfactory resolution of the desired spectrum. A sample of the recorded emission spectra of distilled water and of a 20 microgram per milliliter copper standard are shown in Fig. 1.

The instrument used for the colorimetric analysis of copper was the Evelyn photoelectric colorimeter. A light filter with maximum transmittance at 420 millimicrons was used for all readings.

Mineral Mix Samples Chosen for Analysis

Eight samples of various mineral salts or feeds were selected for this investigation. They were chosen to represent a typical cross-section of mineral mixes. The samples chosen and the sample number of each are given in Table 1. These samples were used throughout the work and will be referred to, henceforth, by sample number only.

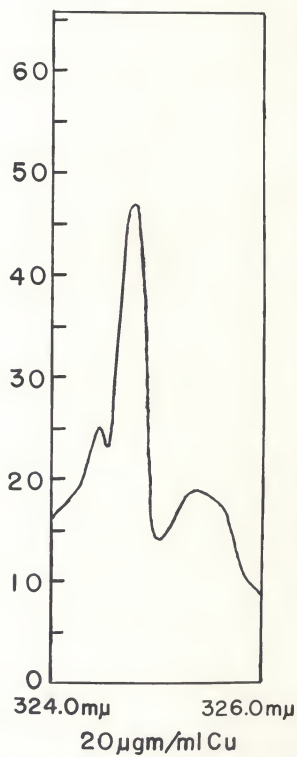
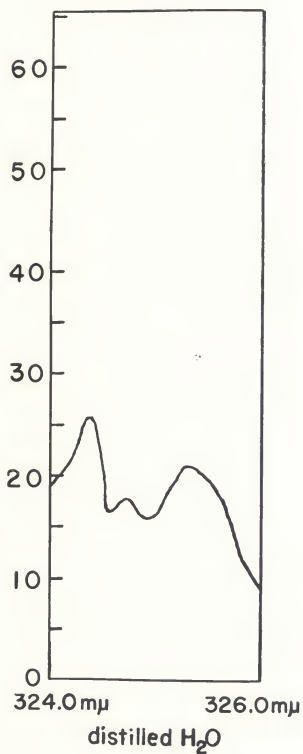


Fig. 1. Recorded flame emission spectra

Table 1. Mineral mix samples chosen for analysis.

Mineral sample	Sample No.
A.A.F.C.O. Check Feed Sample	2B
All-purpose Mineral Salt (Wolf Milling Co.)	924
All-purpose Mineral Feed (Cudahy Packing Co.)	1342
Range Mineral for Sheep (Moorman Mfg. Co.)	1706
Myzon for Beef and Dairy Cattle (Myzon, Inc.)	2011
Three B. Brand All-purpose Mineral	2930
Mello Trace Mineral	2943
Deep Root Fertilizer*	2945

* Composition similar to mineral mixes

Standard Copper Solution

A standard copper solution containing 2000 micrograms per milliliter of copper was prepared by dissolving 2.6624 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in distilled water and diluting to 500 milliliters. All copper standard solutions used in this work were prepared by appropriate dilutions of this original solution.

Comparison of Colorimetric and Flame Photometric Copper Analyses on Mineral Mixes

A preliminary investigation was carried out to determine how the flame photometric analyses of the mineral samples, without separations, compared with an accepted method of analysis for copper. The accepted method selected was the colorimetric procedure which utilizes sodium diethyldithiocarbamate as a complexing agent for copper (Scott, 21). This method is very sensitive for the determination of microgram quantities of copper and proved quite satisfactory for this work. The A.O.A.C. has accepted the carbamate colorimetric

analysis as one of the official methods for the determination of copper in biological materials (18).

The mineral mix samples were placed in a drying oven at a temperature of 105°C for a period of about 20 hours. The samples were then weighed on an analytical balance and transferred to platinum crucibles. Dry weights were recorded. Approximate copper contents of the mineral mixes were known so sample weights were chosen to give copper concentrations of from four to twenty micrograms per milliliter in 100-milliliters final volume. In most cases approximately two gram samples were taken. The samples were then ignited in a muffle for about 16 hours at a temperature of 580°C. Ten milliliters of concentrated hydrochloric acid was added to the platinum crucibles containing the ash and the contents were then transferred quantitatively to 100-milliliter beakers. The samples were then boiled approximately two minutes, evaporated to dryness, and heated on a steam bath for three hours. The residue was moistened with five milliliters of hydrochloric acid, boiled two minutes, and 50 milliliters of distilled water added. After heating the samples for a few minutes they were filtered and washed thoroughly. The solutions were diluted to a final volume of 100 milliliters in volumetric flasks. The ashing procedure carried out here is the official A.O.A.C. method for plant material (18).

A standard curve of micrograms of copper vs. per cent transmittance readings of the Evelyn photoelectric colorimeter was plotted (Fig. 2). Selected amounts of the standard copper solution were placed in 125-milliliter separatory funnels and enough distilled water added to each to make approximately 10-milliliters volume. Five milliliters of 15 per cent citric acid was added and a piece of litmus paper dropped in each of the separatory funnels.

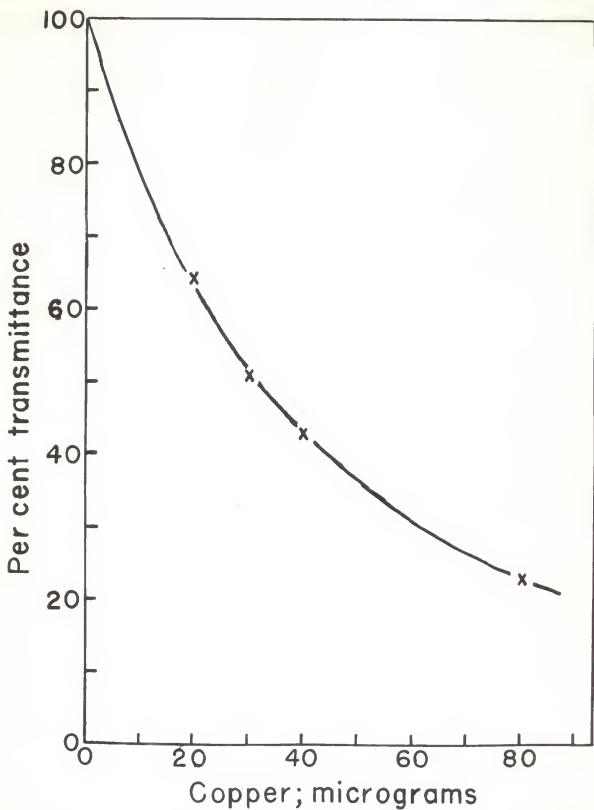


Fig. 2. Colorimetric standard curve for copper

The solutions were then neutralized with 7.5 molar ammonium hydroxide and 10 milliliters of a 0.1 per cent sodium diethyldithiocarbamate solution was added to each. The copper diethyldithiocarbamate was then extracted three times with four-milliliter portions of carbon tetrachloride and collected in 25-milliliter Erlenmeyer flasks. The extracts were filtered through anhydrous sodium sulfate into 25-milliliter volumetric flasks. After washing the filter papers several times with carbon tetrachloride, the flasks were diluted to volume. A blank was determined by treating 10 milliliters of distilled water identically with the standards. The standard curve data were obtained by adjusting the colorimeter to read 10 (100 per cent transmittance) with the blank in the sample cell and zero with the colorimeter lamp off and then taking the readings of the various standards.

Aliquots of the mineral mix solutions, chosen to contain from 10 to 35 micrograms of copper, were then processed exactly as the standards. Each aliquot was diluted to 10 milliliters with distilled water before extracting the copper. This was done so that the blank would apply as nearly as possible to each standard and sample. This procedure assumes that the blank correction is necessary primarily because of copper in the distilled water. The 10 milliliters of distilled water was found to contain enough copper to impart only a faint color to the blank. Duplicate determinations were made on each sample.

Data were obtained for a standard curve for the flame analysis by aspirating copper solutions of known concentrations into the flame and scanning the previously selected wave length range. A standard curve of copper concentration in micrograms per milliliter vs. the height of the recorded copper emission line was plotted (Fig. 3).

As can be seen in Fig. 1, the water emission background shows a slight peak at the wave length of the selected copper line. This was shown to be due

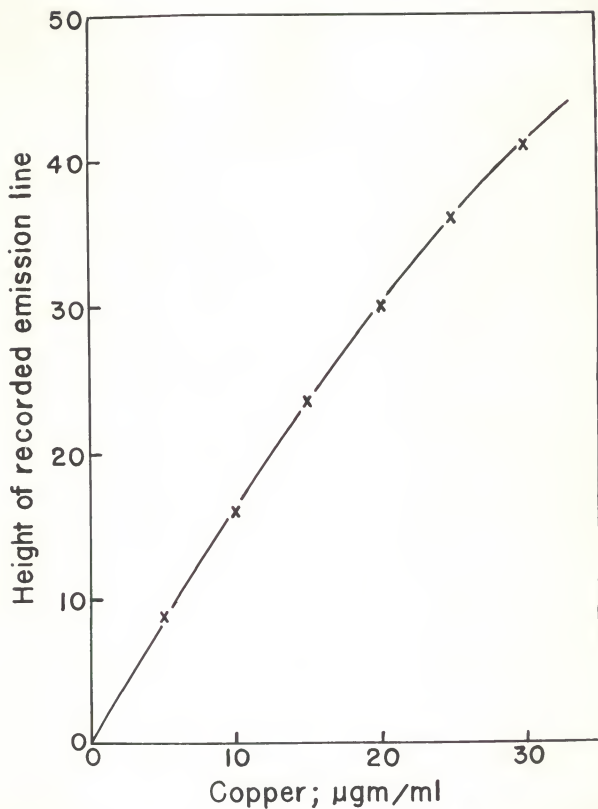


Fig. 3. Flame photometric standard curve for copper

not to copper in the distilled water since an emission curve for doubly distilled water exhibited a similar peak. In order to correct copper emission readings for this background peak, the following procedure was adopted. The height of the background peak as compared to the emission minimum immediately to the longer wave length side of the peak was recorded. This minimum occurred at about 325.0 millimicrons. The heights of all recorded copper emissions also were determined by using this background minimum as a base line. The height of the background peak was then subtracted from all copper emission curve heights to obtain the net copper emission. Use of the recorded flame background from all copper readings as a base line for the determination of the net copper emission automatically compensated for changes in flame background from sample to sample.

The mineral sample solutions which had been prepared were run in triplicate on the flame photometer. The concentration of copper in each sample was determined by taking an average of the net copper emission curve heights and reading from the standard curve.

A technique was adopted to correct for slight changes in the sensitivity of the instrument during a lengthy determination. When a series of samples were run, two or three standard solutions containing copper concentrations approximating that of the samples were run at spaced intervals during the analysis. The readings of these standards were then averaged and, if necessary, used to plot a new standard curve for the desired copper concentration range. This procedure was employed throughout the work.

A tabulation of the results obtained from the colorimetric and flame photometric analysis of the eight mineral mixes is given in Table 2.

A study of the results shows that for each sample the percentage copper as determined flame photometrically is appreciably lower than from the

Table 2. Colorimetric and flame photometric analysis of eight mineral mix samples for copper.

Sample No.	Per cent copper	
	colorimetric	flame photometric
2B	0.060*	0.054
924	0.025	0.021
1342	0.032	0.028
1706	0.027	0.018
2011	0.030	0.022
2930	0.029	0.018
2943	0.474	0.349
2945	0.042	0.035

*Assoc. of Amer. Feed Control Off. collaborative results

colorimetric analyses. Expressed as percentage of "colorimetric copper" recovered by flame analysis, the values run from about 60 to 90 per cent recovery. These results indicated that certain ion or ions present in the mineral samples solutions were causing a repression of the net flame emission of copper. The results indicated a necessity of studying the effects of various cations and anions on copper emission in order to arrive at a satisfactory method of removing the interfering ions.

Interference Studies

Effect of Various Ions on Copper Flame Emission. The interferences on net copper emission caused by the ions present in mineral mixes were next investigated. Solutions containing 20 micrograms of copper per milliliter and various cations and acids at two different concentrations were prepared. The chloride

of each cation was used since the standard copper solution was prepared from cupric chloride. Each solution was analyzed flame photometrically and the apparent concentration of copper determined and recorded. The flame analysis of these solutions was performed in the same manner as described for the mineral mixes. The results are shown in Table 3.

Hydrochloric and nitric acids did not affect copper emission appreciably. Sulfuric acid repressed copper emission slightly. An interesting effect was observed with phosphoric acid. A concentration of 0.1 molar produced only a slight enhancement of copper emission while one molar phosphoric acid caused a large increase in both flame background and net copper emission. Manna, et al. (16) reported a decrease in net copper emission with two molar phosphoric acid in 80 per cent methanol solutions.

Manganese, cobalt, and iron in concentrations up to 200 micrograms per milliliter did not cause any noticeable effect on the emission produced by a 20 microgram per milliliter solution of cupric chloride. At these same concentration levels, sodium, calcium, and magnesium produced only a very slight enhancement of net copper emission while potassium seemed to cause a slightly larger enhancement. A solution containing these seven cations and copper, all at a 20 micrograms per milliliter level, gave a flame photometric copper recovery of 22.2 micrograms per milliliter.

A further study of the effects on copper emission of certain anions was performed. The sodium salts of several anions were added in various amounts to copper concentrations of 5, 10, and 15 micrograms per milliliter. The solutions were analyzed on the flame photometer and the apparent concentration of copper in each determined and recorded (Table 4).

A curious effect upon copper emission was observed in the study of the sodium salts of sulfate, chloride, and monohydrogen phosphate. Sodium sulfate

Table 3. Influence of various cations and acids on the flame emission of 20 micrograms of copper per milliliter.

Cation or acid	Concentration of cation or acid	Copper recovered (ugm/ml)
HCl	0.1 M	19.7
HCl	1.0 "	20.3
HCl	4.0 "	20.8
HNO ₃	0.1 "	19.5
HNO ₃	1.0 "	20.6
H ₂ SO ₄	0.1 "	19.5
H ₂ SO ₄	1.0 "	18.8
H ₃ PO ₄	0.1 "	20.6
H ₃ PO ₄	1.0 "	26.6
Na	20 ugm/ml	20.6
Na	200 "	20.8
K	20 "	21.2
K	200 "	21.4
Ca	20 "	20.6
Ca	200 "	20.8
Mg	20 "	20.3
Mg	200 "	20.8
Mn	20 "	19.7
Mn	200 "	20.3
Co	20 "	19.7
Co	200 "	20.0
Fe	20 "	20.0
Fe	200 "	20.6

Table 4. Influence of the sodium salts of various anions on copper flame emission.

Known copper (micrograms per ml.)	Sodium salt : added to : solution	Concentration : of salt (micro- grams per ml.)	Copper found : (micrograms per ml.)
5.0	Na_2SO_4	200	5.8
5.0	Na_2SO_4	2,000	6.2
5.0	Na_2HPO_4	200	5.0
5.0	Na_2HPO_4	2,000	5.5
5.0	NaCl	10,000	4.3
15.0	Na_2SO_4	200	14.4
15.0	Na_2SO_4	2,000	14.8
15.0	Na_2HPO_4	200	14.2
15.0	Na_2HPO_4	2,000	14.4
15.0	NaCl	10,000	16.3
15.0	NaCl	20,000	16.5
10.0	NaNO_3	2,000	8.9
10.0	Na_2SO_4	2,000	8.7
	Na_2HPO_4	2,000	
10.0	NaNO_3	2,000	9.7
	Na_2SO_4	2,000	
10.0	NaNO_3	2,000	9.0
	Na_2HPO_4	2,000	

and sodium monohydrogen phosphate each caused a slight enhancement upon the emission of a five microgram per milliliter copper solution but appeared to repress the emission of 15 micrograms per milliliter of copper. The effect of sodium chloride was exactly opposite. Sodium nitrate suppressed the emission of 10 micrograms per milliliter of copper. Solutions containing the

sodium salts of two different anions with 10 micrograms per milliliter of copper were run and in each case the net copper emission was suppressed slightly.

The interference studies performed seemed to indicate that the cations investigated either enhance copper emission or have no noticeable effect. The anions appeared to repress net copper emission at copper levels of 10 micrograms per milliliter and above except in the case of phosphoric acid and perhaps the chloride ion. Differences in the effects of certain anions were observed in comparing the results of the acids and the corresponding sodium salts. This is probably caused by a difference in the effects on copper emission of sodium and hydronium ions.

Recovery of Added Copper to a Mineral Mix Solution. The accuracy of an unproven method of quantitative analysis can be checked by several methods. One consists of adding to an unknown sample a definite amount of the substance to be determined and comparing the results with and without the added substance. The difference between the amounts found should equal the amount added.

It was decided to carry out this type of investigation as a further check on the extent of copper emission interferences present in mineral mixes. Sample 2B was selected for the investigation because this sample had been collaboratively analyzed by the Association of American Feed Control Officials. A solution of the sample was prepared which, according to the collaborative results, contained 12 micrograms of copper per milliliter. Twenty-five-milliliter portions of this solution were pipetted into seven separate 50-milliliter volumetric flasks. Appropriate amounts of standard copper solution were added to six of the flasks so they would contain 5, 10, 15, 20, 25, and 30 micrograms per milliliter more copper when diluted to volume than the seventh flask to which no copper was added. The solutions were then analyzed on the flame

photometer. The results (Table 5) which should have shown a constant five micrograms per milliliter increase in copper concentration for the solutions, instead showed increases of from 5.5 to 6.4 micrograms per milliliter. The lone exception was the difference between the samples to which 10 and 15 micrograms per milliliter had been added. A 4.8 microgram per milliliter difference in concentration was observed between these two solutions. A duplication of the investigation showed an increase in recovered increments of copper of over five micrograms per milliliter throughout the series of solutions; therefore, the exception in the first run was overlooked.

The investigation carried out here, as well as the previous work, pointed out very definitely that mineral mixes contain certain cations, anions, or both which cause an appreciable change in the net copper emission in flame photometric

Table 5. Flame photometric recovery of known amounts of copper added to a typical mineral mix (Sample 2B)-micrograms per milliliter.

Copper added :	: Total copper		: Total copper		: Increase over	
	: recovered		: minus copper		: previous	
	:		: in sample*		: solution	
	1st Trial:	2nd Trial:	1st Trial:	2nd Trial:	1st Trial:	2nd Trial:
0.0	5.4	5.4	0.0	0.0	---	---
5.0	10.9	11.0	5.5	5.6	5.5	5.6
10.0	17.0	16.4	11.6	11.0	6.1	5.4
15.0	21.8	21.9	16.4	16.5	4.8	5.5
20.0	28.1	28.3	22.7	22.9	6.3	6.4
25.0	33.8	34.7	29.4	29.5	5.7	6.4
30.0	40.2	---	34.8	---	5.4	---

*Flame photometric results used for the copper content of the sample

analysis. This indicated the necessity of attempting to find a suitable means of removing certain ions from mineral mix solutions to be analyzed or, if necessary, a means of entirely separating copper from the other ions.

Investigation of Anion Removal from Mineral Mix
Solutions with an Anion Exchange Resin

Gehrke and co-workers (8) reported a successful method of removing undesirable anions from fertilizer samples to be analyzed flame photometrically for potassium. They added an anion exchange resin to the fertilizer sample solutions, shook the mixtures for a short period of time, and filtered. The filtrate, to which was added the resin washings, was diluted to a volume and the samples analyzed. The resin which they used was Amberlite IR-4-B (Rohm and Haas Co., Philadelphia, Pa.) which has a high capacity for phosphate. Since the anions investigated in this work had appeared to affect copper emission to some extent, it was decided to attempt the removal of the undesirable anions in the mineral mixes with Amberlite IR-4-B as described.

Since the standard copper solutions were made up with cupric chloride, the chloride ion seemed to be the logical choice to use for the replacement of phosphate and other anions in the mineral solutions. The first step, therefore, was to regenerate the resin to the chloride form. The resin was first exhausted with five per cent sodium hydroxide by the batch process. After washing to remove excess base, the resin was placed in a column and flushed with five per cent hydrochloric acid. Approximately one liter of the acid was used for about 50 milliliters of resin. The resin was then washed with distilled water until no more color throw was observed.

Twenty-five milliliters of sample 2B solution was placed in a 50-milliliter Erlenmeyer flask. Ten milliliters of the wet resin was added and the contents

shaken for about 10 minutes. The mixture was filtered, the resin washed three times with distilled water, and the sample diluted to 50 milliliters in a volumetric flask. A second 25-milliliter portion of sample 2B solution was identically treated. The two resin-treated portions of the sample were then analyzed for copper with the flame photometer. The analysis gave a percentage of copper in the sample of only about one-half of that previously determined colorimetrically. The duplicates agreed almost exactly.

A check was run to determine whether or not some of the copper had been retained by the resin. Twenty-five milliliter portions of standard solutions of both cupric chloride and cupric sulfate were processed exactly as had been the samples. The copper content of the standards before resin treatment was very close to that of the sample 2B solution. The results again showed that about one-half of the copper was retained by the resin. One explanation of the retention of the copper by an anion exchange resin is that, in the presence of the chloride ions on the resin, copper forms a negatively-charged chloride complex which is partially held by the resin.

The use of this method for the removal of interfering anions from solutions to be analyzed flame photometrically for copper did not appear feasible, at least under the conditions employed, so the method was abandoned.

Application of Ion Exchange Column Separations to Copper Flame Analysis

Kraus and Moore (12) reported a method of separating the divalent transition elements, manganese to zinc. They used an ion exchange column containing the quaternary amine polystyrene-divinylbenzene resin Dowex-I (The Dow Chemical Company, Midland, Michigan). The separations were possible because of the varying adsorbabilities on the anion exchange resin of the

negatively-charged chloride complexes which the ions of these elements form in hydrochloric acid. The authors did not report quantitative results pertaining to the separations.

The possibility of the application of this proposed method of cation separation to the separation of copper from other cations present in mineral mixes presented itself. It was decided to investigate the application of this separation technique to copper flame analysis.

The first steps in this investigation were to regenerate a supply of Dowex-I to the chloride form and to construct an ion exchange column. The regeneration was carried out by the same procedure as that outlined previously in this paper for Amberlite IR-4-B. The columns (two were constructed) were made from scrap Pyrex glassware. The columns were designed to have dimensions approximating those of the column used by Kraus and Moore (12). There is no reason to believe, however, that columns of other sizes could not be adapted to the separation. The constructed columns had cross-sectional areas of about 0.5 square centimeter and could contain a resin column height of 25 centimeters. The columns had stopcocks at the lower end and were fitted with ground glass joints at the top. A 125-milliliter separatory funnel was attached to the top of each column. These were for the purpose of containing the eluting agents to be used. The two columns were filled with the prepared Dowex-I. The resin was held in the columns by wads of glass wool below and above. The resin in the columns eventually settled to give column heights of about 24 centimeters.

The next step in the investigation was to determine the optimum concentrations of hydrochloric acid and the volumes of each to be used for the eluting agents. Kraus and Moore (12) reported that manganese and cobalt, both present in mineral mixes, were eluted with four molar or more dilute hydrochloric

acid. Copper was eluted with 2.5 molar hydrochloric acid. From this information it was decided to begin by flushing the columns with six molar hydrochloric acid. The solutions and samples to be run throughout the work also were made six molar with respect to hydrochloric acid. At this level of hydrochloric acid, copper would be strongly adsorbed by the resin. It would be desirable for the copper to be eluted in as sharp a band as possible. It was decided, therefore, to substitute 1.2 molar for 2.5 molar hydrochloric acid to elute copper from the column.

A six molar hydrochloric acid solution containing copper, sodium, potassium, calcium, magnesium, manganese, cobalt, and ferric iron each at a concentration of 20 micrograms per milliliter was prepared. The majority of the cations present to any extent in mineral mixes are included in this list. Five milliliters of the solution were placed on one of the resin columns previously flushed with six molar hydrochloric acid.

The volume of the unfilled column was approximately seven milliliters. The acid in a resin-filled column would probably be completely replaced by a five milliliter sample. This was found to be true as will be shown by the data.

After adding the prepared cation solution to the column, elution was begun using four molar hydrochloric acid for the eluting agent. Three-milliliter portions of the eluate were collected and analyzed flame photometrically for each of the cations in the solution. The analyses were carried out on a semi-quantitative basis. Sodium, potassium, calcium, and magnesium appeared immediately in the eluate. Manganese also was observed in the first three-milliliter fraction but was more concentrated in the second and third fractions. Cobalt concentration reached a peak in the fourth three-milliliter fraction. These six cations were completely eluted from the column with 15 milliliters of the four molar hydrochloric acid. At this time the four molar acid eluting

agent was replaced with 1.2 molar hydrochloric acid. The copper was found almost entirely in the third and fourth three-milliliter portions of 1.2 molar acid. The ferric ion¹ appeared in the eluate before copper was completely eluted from the column. In order to separate copper from the ferric ion, it would probably be necessary to elute copper with a somewhat more concentrated solution of hydrochloric acid. Since the previous work had indicated that iron does not affect copper flame emission to any noticeable extent, the separation of these two elements was not attempted.

Ferrous iron was not used in this separation study. The ferrous ion is less strongly adsorbed on the resin than cobalt (12); so, if present, the former would logically be eluted in the 15 milliliters of four molar hydrochloric acid.

Zinc, which is present in small amounts in mineral mixes, also was not studied. Kraus and Moore (12) reported that zinc is not eluted until considerably after ferric iron, so zinc would probably remain on the column under the conditions used in this work.

In order to insure complete recovery of copper, it was decided to collect the first 20 milliliters of 1.2 molar hydrochloric acid eluate.

The results of this separation study appear in Table 6. The procedure apparently gave complete separation of copper from virtually all cations present in mineral mixes with the exception of the ferric ion.

The resin columns were flushed with approximately 15 milliliters of distilled water after their initial use and then recharged with six molar hydrochloric acid for the next run. This procedure was followed throughout the work.

¹Determined qualitatively only

The next step in this investigation was to determine the completeness of the copper recovery. A standard solution containing 20 micrograms of copper per milliliter in six molar hydrochloric acid was prepared. Aliquots containing 20, 40, 60, and 80 micrograms of copper plus enough six molar hydrochloric acid to make a total volume of approximately five milliliters were added in turn to the columns. Fifteen milliliters of four molar hydrochloric acid was eluted and discarded. Twenty milliliters of 1.2 molar hydrochloric acid eluate was then collected, evaporated to somewhat less than five milliliters, and diluted to exactly five milliliters with distilled water. These solutions

Table 6. Separation of copper from a mixture of cations by means of an anion exchange resin column. (Arbitrary concentration units)

Molarity of : Three-ml.:		Concentration of cation in eluate							
HCl eluting : fraction :		Na :	K :	Ca :	Mg :	Mn :	Co :	Cu :	
agent :	of eluate :								
4.0	1st	12	7	11	14	6	0	0	
4.0	2nd	13	8	11	14	14	0	0	
4.0	3rd	4	2	4	5	15	5	0	
4.0	4th	0	0	0	0	2	15	0	
4.0	5th	0	0	0	0	0	3	0	
1.2	6th	0	0	0	0	0	0	0	
1.2	7th	0	0	0	0	0	0	2	
1.2	8th	0	0	0	0	0	0	27	
1.2	9th	0	0	0	0	0	0	19	
1.2	10th	0	0	0	0	0	0	1	
1.2	11th	0	0	0	0	0	0	0	
1.2	12th	0	0	0	0	0	0	0	

were then determined for copper with the flame photometer. The results showed slightly over 100 per cent recovery in every case. This implied that complete recovery was achieved for these amounts of copper and also indicated the necessity of running a blank.

A series of blanks were run to determine an "average" blank to be applied as a correction on the mineral mix samples to be run next in this work. The blanks were run by carrying out the same procedure of column elution as had been done with the standard solutions previously, except with no added copper. The evaporation step also was included. The blanks were compared with standards on the flame photometer. An average of 0.3 micrograms per milliliter in the five-milliliters final volume was found.

The eight mineral mix solutions prepared earlier were made six molar with respect to hydrochloric acid by diluting one to one with 12 molar hydrochloric acid. Five milliliters of each of these new solutions were added in turn to the resin columns and treated according to the elution procedure which had been developed previously in this work. This consisted of first eluting with 15 milliliters of four molar hydrochloric acid which was discarded and then collecting 20 milliliters of 1.2 molar acid eluate. The 20-milliliter volumes were evaporated to somewhat less than five milliliters and diluted to exactly five milliliters with distilled water. These solutions were then determined for copper by comparing with standard copper solutions on the flame photometer. The readings were corrected for the previously determined blank in calculating the per cent copper in the samples. Two separate determinations were made on each sample with the exception of sample 2B which was run six times. The results are given in Table 7.

Table 7. Flame photometric determination for copper in mineral mixes following the ion exchange column separation of copper from other cations.

Sample no.	Per cent copper found	
	: Colorimetric*	: Flame photometric
2B	0.060	0.060, 0.057, 0.059
		0.059, 0.056, 0.058
		Ave. 0.058
		S.D. \pm 0.0013
924	0.025	0.025, 0.025
		Ave. 0.025
1542	0.032	0.033, 0.029
		Ave. 0.031
1706	0.027	0.023, 0.027
		Ave. 0.025
2011	0.030	0.023, 0.027
		Ave. 0.025
2930	0.029	0.020, 0.022
		Ave. 0.021
2943	0.474	0.377, 0.372
		Ave. 0.375
2945	0.042	0.043, 0.039
		Ave. 0.041

* Colorimetric results from Table 2

DISCUSSION

The investigation of the effects of various cations and anions present in mineral mixes on copper flame emission performed in this work pointed out the necessity of isolating copper from as many of these ions as possible before determining copper. As a general rule, the cations seemed to enhance copper emission and the anions exhibited a repressing effect. This was pointed out previously.

The cation separation technique employing an anion exchange resin column presented in this work gave a very effective means of isolating copper from all other cations except ferric iron.

Since an anion exchange resin was used for this separation, it was suspected that the anions in the mineral solutions would be replaced by the chloride ions of the column. A qualitative check was made on the sulfate ion. Barium sulfate was visibly precipitated from each of the eight mineral mix solutions upon addition of barium chloride. After the resin column separations were carried out, added barium chloride produced no precipitate in any of the solutions. It is probable that all other anions also were replaced, at least to a considerable extent, by chloride. The ultimate possibility of this separation technique would be to recover the copper from the column as cupric chloride free from virtually all other ions.

A preliminary study had shown the flame photometric analysis for copper in the mineral mixes without any separations being made to give lower results than those obtained colorimetrically. This indicated that the copper emission was being repressed. The results obtained in the flame photometric recovery of known added amounts of copper to a mineral mix solution showed over 100 per cent recovery. This seemed to indicate an enhancement of copper emission by some ion or ions present in the solution. An observation of interest was made in connection with this apparent disagreement of results. A five-milliliter portion of sample 2B was added to one of the resin columns and eluted according to the devised procedure. Instead of collecting only the 20 milliliters of 1.2 molar hydrochloric eluate, the 15 milliliters of four molar acid was also collected. This total volume was evaporated and made to exactly five milliliters. The solution would contain virtually all of the cations from the sample; however, the anions would have been replaced by chloride ions. A flame

photometric analysis of the sample now gave a copper content higher than that observed colorimetrically for sample 2B. This phenomenon seemed to substantiate further the idea that copper emission is enhanced by the cations present in mineral mixes and is repressed by the anions. Apparently both effects are present but the anion effect must be greater than the cation effect in the samples studied.

The quantities of copper in the five-milliliter volumes of the mineral mix samples taken for the resin column treatment ranged from about 10 to 40 micrograms. Previous study had shown that no loss of copper occurred when up to 80 micrograms of copper was eluted through the column. There is no reason not to believe that even considerably larger amounts of copper could be successfully recovered. It would probably prove advantageous to use larger amounts than those taken for this work because the evaporation step might possibly be eliminated. This would save considerable time.

The volumes of the two eluting agents used in the process need not be exact. The important step is to change the eluting agent from four molar to 1.2 molar hydrochloric acid after the elution of the majority of the cations which appear in the eluate first and before the elution of copper.

During the elutions, the stopcocks on the columns were completely opened and the eluting agents allowed to flow at their maximum rate. The resin columns offered enough resistance to flow that the flow rate did not exceed about 0.4 milliliters per minute nor did it fall much below this.

The two columns were used for the entire investigation without regeneration of the ion exchange resin. The cations are washed from the column during each separation; so, were it not for the retention of the anions from the mineral mix samples by the resin, the columns could be used indefinitely. During the work performed here, the presence of anions other than chloride in the eluate

was not observed. The previously mentioned tests for sulfate were made toward the latter part of the work. It would, of course, be necessary to eventually regenerate the resin to the chloride form in order to keep undesirable anions out of the solutions to be determined on the flame photometer.

The results of the flame analysis of the eight mineral mix solutions for copper by using this separation technique gave excellent precision. No reason can be given for the poor agreement between the colorimetric copper analysis and the results obtained flame photometrically using the ion exchange separation technique in the case of samples 2930 and 2943. It is possible that personal or experimental error could account for at least some of the disagreement.

Since many of the transition elements important in biological materials form negatively-charged chloride complexes in various concentrations of hydrochloric acid, the extension of the separation technique studied in this work to the separation or isolation of other elements is feasible. It perhaps might be possible to devise a separation scheme in which a series of elements could be isolated for flame determination. Manganese, cobalt, and iron are three elements which could very likely be fitted into the scheme.

CONCLUSIONS

This investigation has shown that copper flame emission is influenced by the presence of various cations and anions present in mineral mixes.

A procedure for separating copper from the bulk of a mineral mix solution has been developed. The procedure involves an anion exchange resin column separation. Copper is collected from the column as cupric chloride. Ferric iron apparently is the only contaminating ion present to any appreciable extent in the collected fraction of eluate. Iron does not noticeably affect copper flame emission.

Since copper is collected from the column as the chloride without any detectable loss of the copper, standard solutions of cupric chloride need not be processed before flame analysis as are the samples. This saves considerable time.

Through the use of this separation technique prior to the flame photometric copper analysis of mineral mix solutions, excellent precision has been found. The accuracy was quite acceptable in most cases; however, low recovery of copper was observed for a few samples. Further investigations should be performed in an effort to determine the cause of these low results.

Techniques have been developed which correct for changes in flame background and slight variations in spectrophotometer sensitivity.

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FLAME PHOTOMETRIC ANALYSIS OF COPPER
WITH ION EXCHANGE SEPARATION OF INTERFERING IONS

by

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This research was conducted to study the flame photometric analysis of microgram quantities of copper in mineral mixes. The investigation consisted of first determining the effect on copper flame emission of various ions present in mineral mixes and then finding a method for the removal of these interfering ions.

Cations were found, as a rule, to cause an enhancement of copper emission while anions usually caused a repression. These interferences were studied by adding various amounts of a particular ion to one or more concentrations of copper and determining the copper emission as compared to copper standards.

The flame photometric analyses for copper in the mineral mixes in this work gave low results as compared to an accepted colorimetric method. Flame photometric recovery of known amounts of copper added to a mineral mix gave high results. This difference of behavior was attributed to a combination of enhancement and repression effects by the ions present in the solutions.

A procedure was developed which gave a simultaneous removal of all undesirable anions and cations except ferric iron from mineral mix solutions to be analyzed flame photometrically for copper. The procedure involved an anion exchange resin column elution with various concentrations of hydrochloric acid. Copper forms a negatively-charged chloride complex in hydrochloric acid which was adsorbed rather strongly on Dowex-1, the resin used in this work. The majority of the cations in a mineral mix solution were found to be eluted before copper while the anions remained on the column after the removal of copper as the chloride.

Since the standard copper solutions in this work were prepared from cupric chloride, the flame analysis of the copper from the mineral mixes as the chloride eliminated the necessity of treating the standard solutions in any manner.

The use of a Spectral Energy Recording Adapter and Brown Recorder in the copper determinations gave an automatic correction for changes in flame background. The copper emission values were determined by using the recorded flame background adjacent to the copper line as a base line.

Slight changes in instrument sensitivity during a lengthy series of determinations can give erroneous results. These were corrected by taking flame emission recordings of several standard copper solutions at spaced intervals during the copper determinations. Averages of these standard solution readings were used to plot a new standard curve and the average reading of each sample was used to determine copper content from this new standard curve.

Flame photometric determinations for copper in mineral mixes, using the ion exchange separation technique, gave results much closer to the colorimetric analyses than did the flame analyses without any separations. The agreement was quite good in most cases. The proposed method was found to give very good precision on all samples studied.