



Effects of anions on magnesium flame emission in flame photometry
by Glen F Anderson

A THESIS Submitted to the Graduate Faculty IN partial fulfillment of the requirements for the degree
of Master of Science in Chemistry at Montana State College
Montana State University
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Abstract:

This investigation was prompted by the conclusive results obtained in studying the anionic influence on the flame intensities of calcium emission by flame photometry (1). Although little or no resolution was exhibited by oxy-acetylene flame on magnesium as was found with calcium, the oxygen-hydrogen flame showed excellent resolution for magnesium. Perchlorate ion enhances the flame emission, whereas phosphate ions depress the values in the analysis of magnesium. The arsenate, sulphate, borate, dichromate also exhibit a depressing action. It has also been observed that when any two or more of the above anions are present in the same solution, some knowledge of the anionic system is necessary for an accurate determination of magnesium by flame photometry.

EFFECTS OF ANIONS ON MAGNESIUM
FLAME EMISSION IN FLAME PHOTOMETRY

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Chairman, Examining Committee

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I. ABSTRACT

This investigation was prompted by the conclusive results obtained in studying the anionic influence on the flame intensities of calcium emission by flame photometry (1). Although little or no resolution was exhibited by oxy-acetylene flame on magnesium as was found with calcium, the oxygen-hydrogen flame showed excellent resolution for magnesium. Perchlorate ion enhances the flame emission, whereas phosphate ions depress the values in the analysis of magnesium. The arsenate, sulphate, borate, dichromate also exhibit a depressing action. It has also been observed that when any two or more of the above anions are present in the same solution, some knowledge of the anionic system is necessary for an accurate determination of magnesium by flame photometry.

II. HISTORY AND DEVELOPMENT

The urgent need for extremely rapid and accurate sodium determinations on large numbers of samples led to the development of the flame photometer. Previously existing methods employed were rather time consuming and required considerable sample preparation particularly in cases where only traces of sodium were present.

The groundwork for the development of flame photometry was set down by Lundegardh in his book (9), describing a method of spectro-chemical analysis which included a listing of lines characteristic of some 34 elements in 1934.

Although instrumentation was developed and commercially available in Germany prior to use in this country, description of the essentials for analysis of lines describing the use of air-acetylene flame first appeared in this country in 1944, (2).

The first really successful analytical procedure in America was developed and published in 1945 by R.B. Barnes et al (2), whereby it was readily demonstrated that any of the characteristic radiations, if isolated by passage through proper filters, will, upon striking a photosensitive element, give rise to an electrical impulse which is a function of the quantity of the respective metal present in the sample.

In the past ten years considerable attention has been directed to the improvement of instrumentation and technique, thereby enhancing the scope of this rapid, accurate and relatively simple approach to analysis. It is reasonable to assume that the surface has only been touched in this field.

III. INTRODUCTION

Although instrumentation consumed most of the time devoted to flame photometry in the early years since Lundegardh (9), proposed and established his early method, considerable work has been done in this field during the past ten years. Quantitative aspects of both cation and anion influence have been investigated and shown to affect the intensities of many characteristic flame emissions. Considerable investigation has been done with the cationic influence, but the search into the anionic effects has been limited (3-5-6-7-8-11). Recent studies (1), (6), (8), have established the necessity for accounting for anionic effects in accurate quantitative work.

This paper reports on some anionic effects on magnesium analysis by flame photometry. Data obtained by adding increments of some ten acids to a standard magnesium chloride solution are presented.

IV. EXPERIMENTAL

In this investigation, a Beckman D.U. spectrophotometer Model 9200 with photomultiplier attachment was used. Oxy-hydrogen flame dispensed through a number 4020 hydrogen atomizer was the excitation source, except for a small portion of the experiment devoted to a comparison of emissions when an oxy-acetylene flame was used.

Relative readings were made with standard magnesium chloride solutions containing increments of various acids. The magnesium chloride standard was prepared by dissolving magnesium ribbon in hydrochloric acid, evaporating to dryness and diluting with distilled water to produce a 0.02M magnesium chloride stock solution. This in turn was used to prepare the individual standards by proper dilution to the various concentration of the acids as indicated.

Magnesium has two lines at wave lengths of 285.2 mu. and 371 mu. These wave lengths are for magnesium oxide bands. Resolution at either wave length was good with possibly a lesser background interference at the 371 mu. setting, and the latter was arbitrarily chosen for this experiment. Other instrument conditions included a slit width of 0.07 mm, with a reading of 100 on the transmittancy scale for a standard 0.004 M magnesium chloride solution. This reading was obtained by adjustment of the monochromatic sensitivity control. Gas pressures were 4 P.S.I. for hydrogen and 12 P.S.I. for oxygen. Optimum conditions were established for each separate operation with the needle valve in the hydrogen line provided on the instrument. During the course of sample runs constant reference to the established standard conditions was made. The necessary minor adjustments

were facilitated by the sensitivity control. Needle drift was constantly zeroed by the dark current control. For the wave length 371 μ , the blue sensitive photomultiplier tube was used. Instrument warmup procedure included a ten minute period with the selector switch at "CHECK". Another ten minutes were allowed, after switching to ".1" and the battery box sensitivity turned to "Full". The oxygen and hydrogen pressures were low at lighting and then brought to operating pressures, with distilled water being aspirated to avoid excessive tip heat to the atomizer.

The highly sensitive instrument conditions, when oxy-hydrogen flame was used for magnesium excitation, made reproducible results impossible when even the slightest light leaks existed. Reproducibility was ultimately accomplished by covering the "pull arm" opening for the filter slide with a strip of black masking tape. This minute source of light did not cause serious needle fluctuation with oxy-acetylene flame.

With instrument conditions established for a reading of 100 on the transmittancy scale as described, slit width adjustment was made to 0.063 mm to give a reading of 80. All anionic effects were studied at the 100 reading or 80 reading as conditions warranted. The setting at 80 permitted an increase or decrease to be noted.

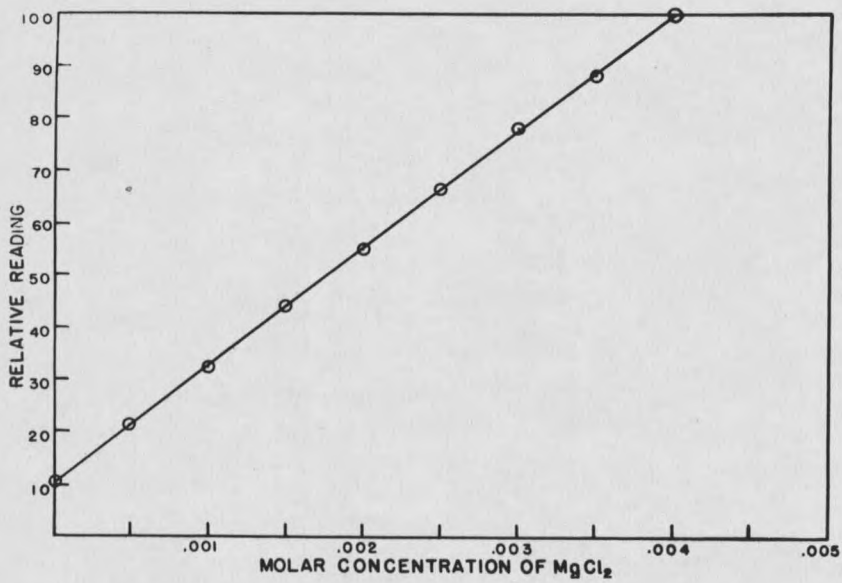


Figure 1. Relative Emission Intensities of Pure Magnesium Chloride Solutions.

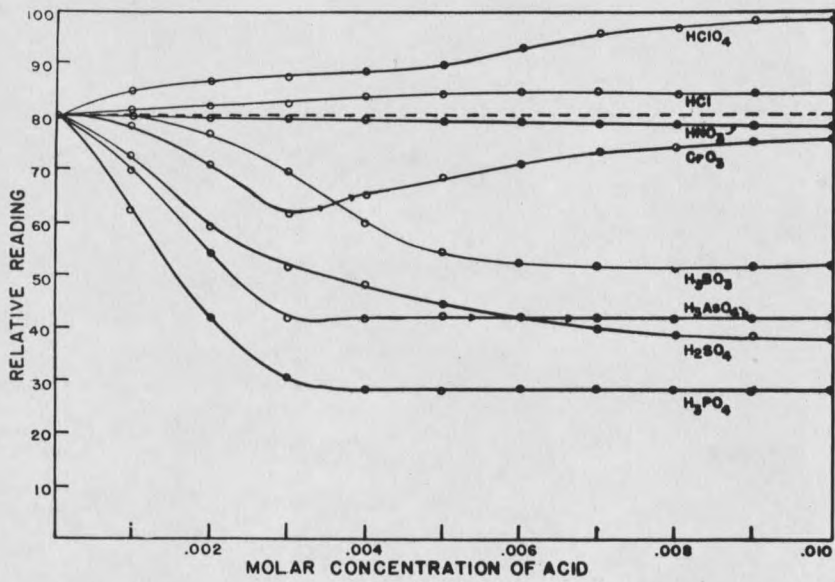


Figure 2. Cursory Examination of Various Acid Concentrations on Intensity of Magnesium Oxide Emission.

V. DISCUSSION

Figure #1 shows the resolution of magnesium chloride solution with oxygen-hydrogen flame emission and the feasibility of magnesium analysis at low concentrations with flame photometry.

A cursory examination of the addition of various acids to magnesium chloride solution is shown in Figure #2. The relative insignificance of effects on magnesium chloride by either hydrochloric acid or nitric acid indicates the improbability of hydrogen ion influence on the magnesium flame emission.

The depressing effect noted for phosphate, arsenate, sulfate and borate ions are highly significant. For instance, as in the case of phosphate ion, a magnesium to phosphate ratio of 2:1 reduces the relative reading for magnesium nearly 50%. Perchlorate ion is unique in its action and enhances the reading sufficiently to warrant a more detailed examination as do the depressants.

Figure #3 shows the results of data taken when various levels of magnesium chloride were used and increasing amounts of sulfuric acid added. Instrument conditions were established at the reading shown for the 0.004 M magnesium chloride level and zero acid concentration and maintained when data were taken at the remaining levels. The results indicate that a molecular ratio may be in effect. A maximum effect seems to be established in all cases by the time the ratio of magnesium to sulfate of 1:2 has been reached, noted by the dotted line.

Arsenic acid increments when added to various constant concentrations of magnesium chloride as shown in Figure #4 definitely establish a constant

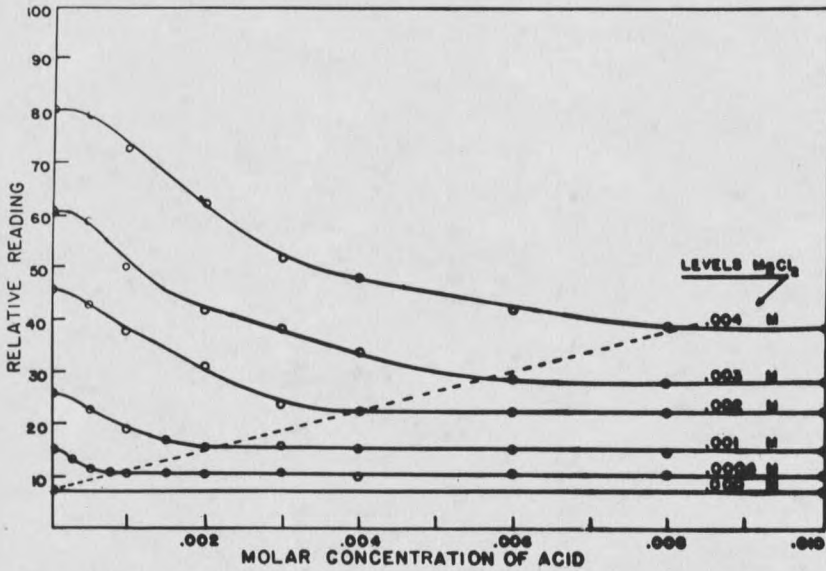


Figure 3. Effect of Varying Sulfuric Acid Concentrations at Different Magnesium Chloride Levels on Intensity of Magnesium Flame Emission.

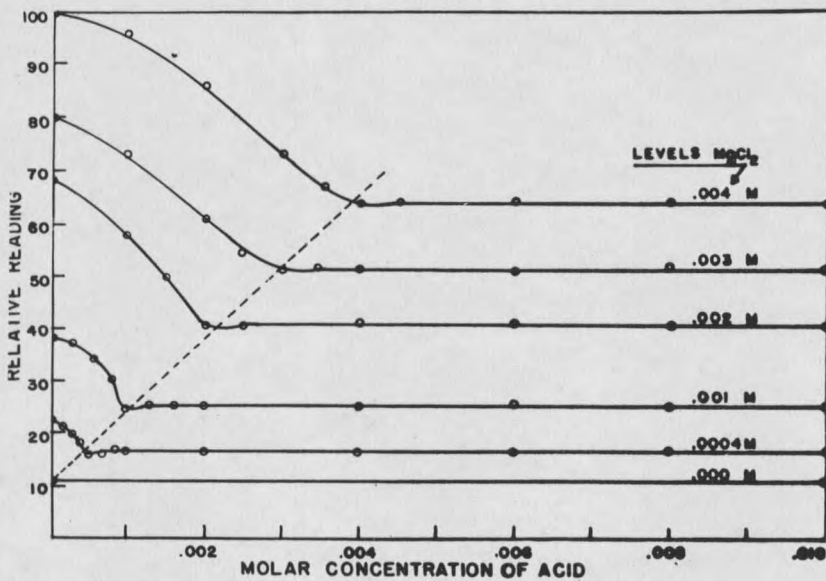


Figure 4. Effect of Varying Arsenic Acid Concentrations at Different Magnesium Chloride Levels on Intensity of Magnesium Flame Emission.

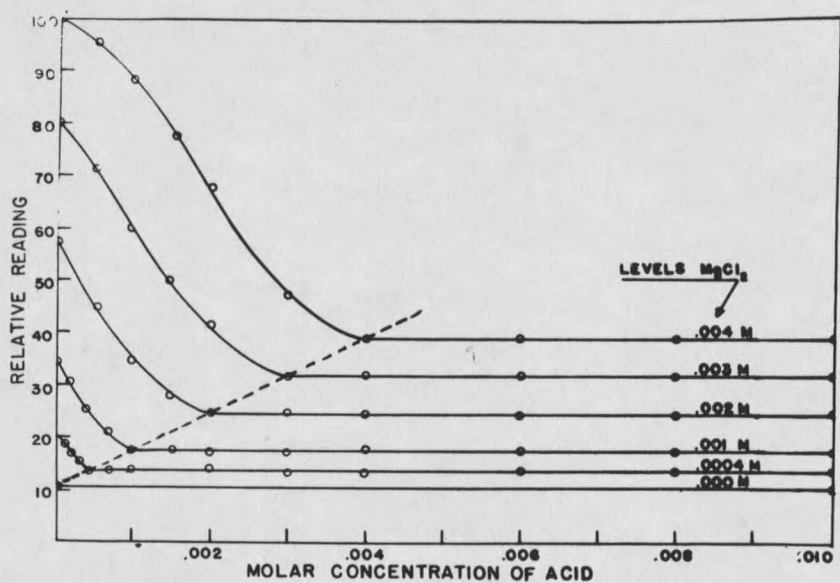


Figure 5. Effect of Varying Phosphoric Acid Concentrations at Different Magnesium Chloride Levels on Intensity of Magnesium Flame Emission.

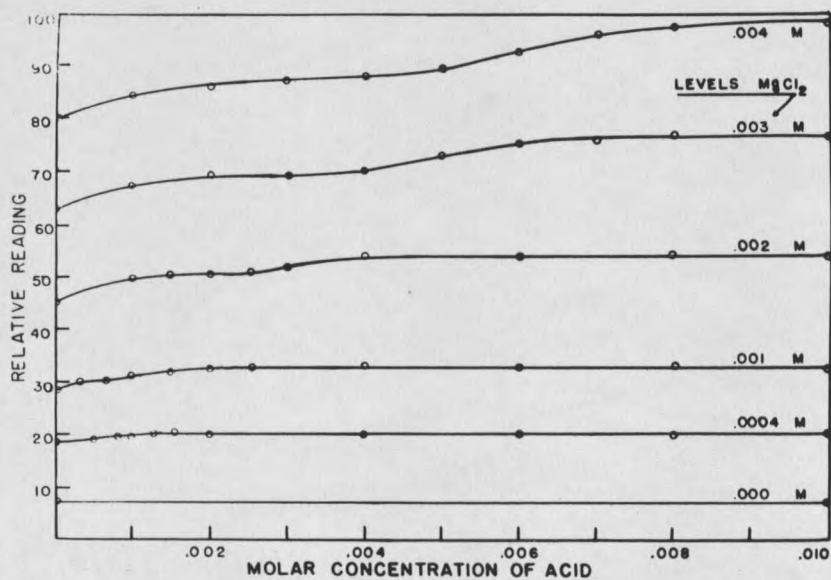


Figure 6. Effect of Varying Perchloric Acid Concentrations at Different Magnesium Chloride Levels on Intensity of Magnesium Flame Emission.

value but only after a very slight increase in readings in each case just after a minimum value has been attained. This minimum value appears to occur at a magnesium to arsenate ratio of 1:1. Instrument conditions were established for 0.004 M magnesium chloride to read 100 at a slit width of 0.07 mm for all curves.

Figure #5 illustrates a detailed examination of the effects of the phosphoric acid, the most depressant of the acids used in its action. As indicated previously with both sulfuric and arsenic acids, phosphoric acid seems to present a molecular ratio at the minimum reading. The magnesium to phosphate ratio of 1:1 is noted by the dotted line in the graph. Standard 0.004 magnesium chloride was read with the instrument readings at 100 on the transmittancy scale at 0.07 mm slit width.

Figure #6 verifies the double rise shown in the cursory examination for the perchloric acid curve. In all cases a rise is noted early for perchlorate ion with a leveling off, followed by a second rise to a near maximum. A molecular ratio does not appear as definite with the perchloric acid curve as was indicated with the depressants, although beyond the magnesium to perchlorate ratio of 1:2 the enhancement is for all practical purposes negligible.

The question now arises as to the effect on magnesium chloride flame emission when the various acids are together in the solution. To determine whether two depressants in solution with magnesium would further depress the readings by additive effect, or whether two depressants would compete, a series of runs incorporating combinations were made.

Figure #7, shows the effect on magnesium flame emission by adding

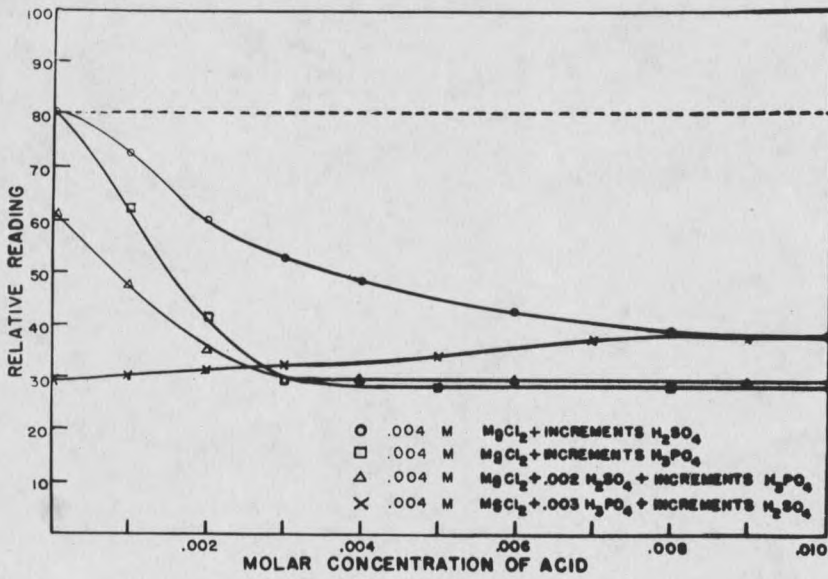


Figure 7.

Effect of Sulfuric-Phosphoric Acid Mixture on Intensity of Magnesium Flame Emission.

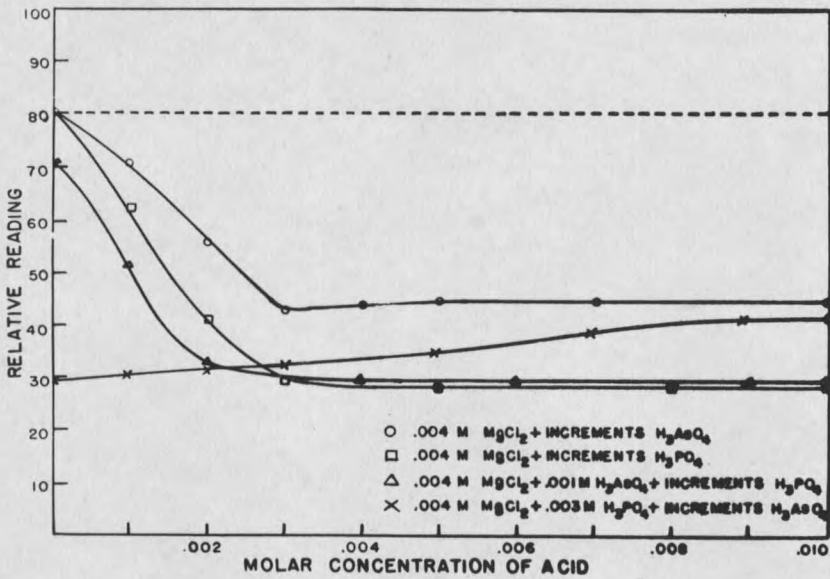


Figure 8.

Effect of Arsenic-Phosphoric Acid Mixture on Intensity of Magnesium Flame Emission.

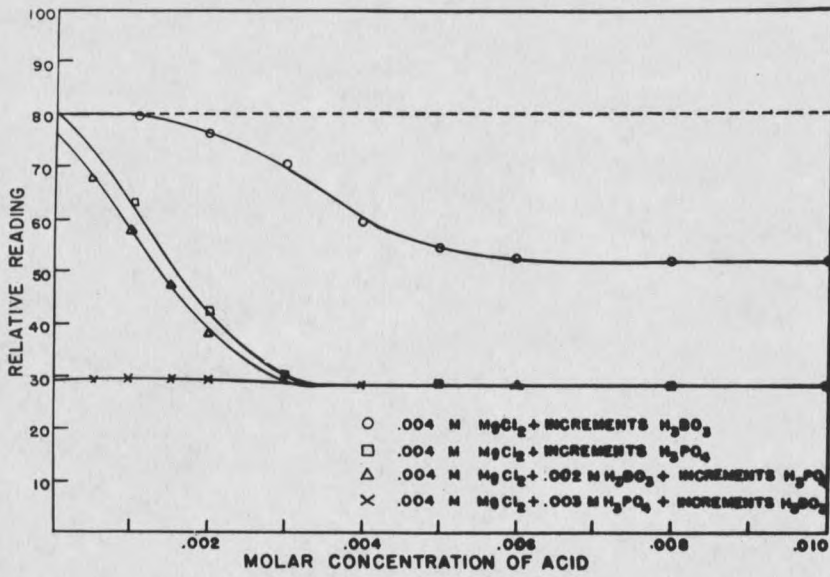


Figure 9.

Effect of Boric-Phosphoric Acid Mixture on Intensity of Magnesium Flame Emission.

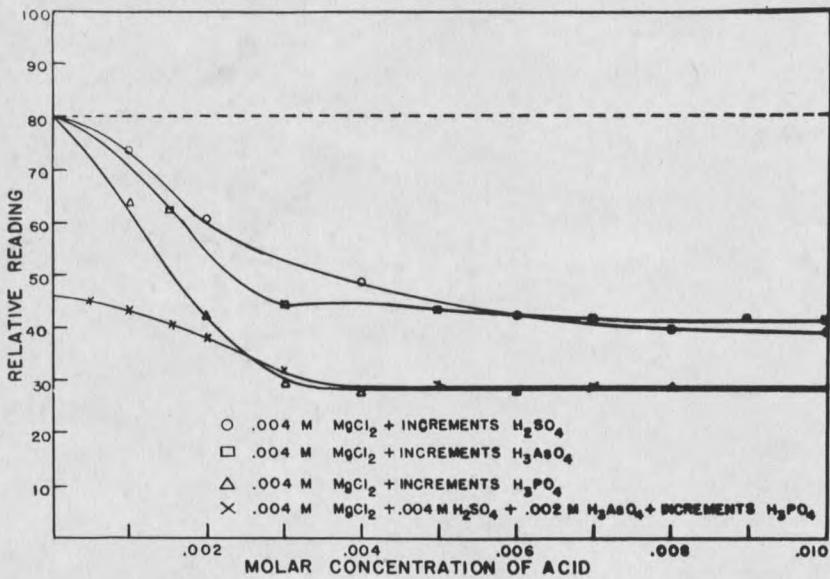


Figure 10.

Effect of Sulfuric-Arsenic-Phosphoric Acid Mixture on Intensity of Magnesium Flame Emission.

increments of phosphate ion to a constant mixture of magnesium chloride and sulfuric acid in one case, and adding increments of sulfate ion to a constant mixture of magnesium chloride and phosphate ion in the second situation. The results show that the depressing effect of sulfate ion does not add to the depressing effect of phosphate ion, but rather the effect is a competing one determined ultimately by the ion existing in excess in the solution. Further it shows that the readings approach the same minimum value for the ion in excess, as was obtained when that ion was the sole depressant.

Figure #8, wherein phosphoric acid and arsenic acid are used in combination with a solution of magnesium chloride, follows essentially the same pattern as shown in Figure #7. It should be noted however, that as the increments of arsenate ion are added to the constant mixture of magnesium chloride and phosphate ion, the depressant effect of phosphate was exerted for a considerable time and not until the arsenate ion was increased to nearly three fold that of phosphate, did the curve approach the minimum for arsenate.

Figure #9 illustrates the effect of the strongly depressant phosphate ion in combination with a mildly depressant borate ion. In the case of the increasing amounts of borate, added increments of borate never overcome the original depressing action of the phosphate ion even at the borate to phosphate ratio of 3:1 in favor of the borate ion.

Figure #10 illustrates the answer to the question as to the effects of a combination of three depressants in solution with magnesium chloride. As expected, the effects are still competitive with the phosphate minimum

