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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EFFECTS OF ANIONS ON MAGNESIUM FLAME EMISSION IN FLAME PHOTOMETRY

by

Glen F. Anderson

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

Approved:

Head, Major Department

Chairman, Examining Committee

Dean, Graduate Division

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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.
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.
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 1020 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 wavelengths of 285.2μm and 371μm. These wavelengths are for magnesium oxide bands. Resolution at either wavelength was good with possibly a lesser background interference at the 371 μm 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 0.001M 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 oxyhydrogen 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 0.001 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 M 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
Figure 11. Effect of Sulfuric-Arsenic Acid Mixture on Intensity of Magnesium Flame Emission

Figure 12. Effect of Perchloric-Phosphoric Acid Mixture on Intensity of Magnesium Flame Emission.
Figure 13. Effect of Perchloric-Arsenic Acid Mixture on Intensity of Magnesium Flame Emission.

Figure 14. Effect of Perchloric-Sulfuric Acid Mixture on Intensity of Magnesium Emission in Oxygen-Hydrogen Flame.
being attained as the increments of phosphoric acid are added. It is interesting to note that the sulfate and arsenate ions present a partially additive action as illustrated by the initial reading for the multiple combination curve marked by the "x" points.

Figure #11, showing the effects of sulfuric acid and arsenic acid provides no new evidence but reaffirms that heretofore brought forth. The close proximity of the levels extended beyond the minimum point makes the results more difficult to illustrate, however the approach to the excess acid line is noticeable.

The effects of the depressant acids in combination with the enhancing perchloric acid are shown in Figure #12, Figure #13 and Figure #14.

Figure #12 establishes a purely competitive nature of the acids. Perchloric acid maintains a higher reading for the same concentration of phosphoric acid than exists in the absence of the perchloric acid, however, as before, the phosphoric acid minimum value is reached. The attainment of this minimum however is at a phosphoric acid concentration almost double that required to reach the minimum without the perchloric acid.

Figure #13 follows the pattern as established above in Figure #12. However, the depressant nature of the arsenate ion is not sufficient to overcome completely the enhancing action of the perchloric acid within the concentration limits illustrated.

Figure #14, whereby perchloric acid and sulfuric acid are used in combination with magnesium chloride adds nothing new.

In the cursory examination of the acids, Figure #2, chromic acid reacted in a manner that was perhaps unexpected. Although no further
Figure 15. Effect of Perchloric-Chromic Acid Mixture on Intensity of Magnesium Flame Emission.

Figure 16. Effect of Perchloric-Sulfuric Acid Mixture on Intensity of Magnesium Emission in Oxygen-Acetylene Flame.
Figure 17. Effect of Perchloric-Sulfuric Acid Mixture on Intensity of Calcium Emission in Oxygen-Acetylene Flame.

Figure 18. Effect of Perchloric-Sulfuric Acid Mixture on Intensity of Calcium Emission in Oxygen-Hydrogen Flame.
Figure 19. Effect of Perchloric-Phosphoric Acid Mixture on Intensity of Calcium Emission in Oxygen-Hydrogen Flame.
examination was made at this time, the depressing action to a minimum and then a rise in the curve should be further investigated in light of the pyroion postulate made by Baker & Johnson (1). Figure #15 illustrates the results when chromic acid was used in combination with perchloric acid with a purely competitive action for the available ions being shown.

To attempt to shed more light into the nature of the results described thus far, an oxy-acetylene flame was used to excite the mixtures of sulfuric-acid-perchloric acid in combination with magnesium chloride. (These solutions excited with oxy-hydrogen flame were illustrated in Figure #14.) These results as shown in Figure #16 follow the features of the hydrogen flame exactly, differing only in the extent of depressing or enhancing values of the individual acids on the standard magnesium flame emission.

In light of the work previously done with the calcium emission when excited with oxy-acetylene flame, solutions of calcium chloride with mixtures of perchloric-sulfuric acids were subjected to oxy-acetylene flame. The anomalous results obtained by Baker & Johnson (1), were reaffirmed as shown in Figure #17.

However these solutions subjected to the oxy-hydrogen flame, Figure #18, showed no anomaly, but as in other cases discussed, portrays the purely competitive nature of the ions. In addition, the increased extent of depressing action of the sulfate ion in the oxy-hydrogen flame is again apparent. The perchlorate ion however is noticeably lower in its enhancement values, in the oxy-hydrogen flame and attains its maximum value at relatively small concentrations.

The anomaly shown, similar to Figure #17, with perchloric-phosphoric
acid mixtures on calcium chloride by Baker & Johnson (1), is not observed when the solutions are subjected to oxy-hydrogen flame, Figure #19.
VI. ANALYTICAL SIGNIFICANCE

The evidence establishes that a working curve for the determination of magnesium by flame photometry with oxy-hydrogen flame is feasible. However at the low concentrations of magnesium that can be determined in this manner, it is of paramount importance that the general composition of the solution being excited be noted. A file of working curves taking into account the depressant effect of each of the several anions may be prepared, and then selected for the anion whose concentration is predominant. To facilitate the problem however, should the anions present not exceed the magnesium to anion ratio of 1:1, addition of phosphate ion beyond the magnesium to phosphate ratio of 1:1 will permit the phosphate curve to be used for all situations.
VII. THEORETICAL IMPLICATIONS

A summary of the data presented poses many problems that are worthy of note and inquiry. Why, for instance, is a greater depressing action by some anions caused on either magnesium or calcium emission when oxy-hydrogen flame is used than when an oxy-acetylene flame is used? Also, why is the reverse true in the two flames when exciting calcium as noted in the Figures #17 and #18 with perchloric acid, in that a lesser increase is shown for the oxy-hydrogen flame as compared to the oxy-acetylene flame? Why is there an apparent leveling effect in the perchloric acid curve, Figure #6, followed by a second rise to a near maximum? Why does the chromic acid curve, Figure #2, depress to a minimum value and then rise as shown, within the concentrations limits used? The same behavior is noted but more limited in the case of arsenic acid, Figure #2. Also at very high concentrations beyond the limits employed in this work, most all of the acids show this tendency to return.

Two other points of interest may be noted. Why did the initial reading of the curve through the "x" points in Figure #10 originate at the indicated level? And secondly, why was it impossible to duplicate readings at the start of the experiment with oxy-hydrogen flame until light leaks were reduced beyond that point that permitted operation with oxy-acetylene flame at identical instrument sensitivities?

The last two points may be explained more readily than the problems posed earlier. With regard to the light leaks, the problem appears to be one of signal to background ratio. In the oxy-acetylene flame this ratio obviously was higher than for the oxy-hydrogen flame in the excitation of
magnesium. Thus, an equivalent amount of spurious light was not sufficient to change the given ratio to the point of interference in the oxy-acetylene flame. The increase in background with the smaller ratio attained by the oxy-hydrogen flame was sufficient however to require elimination of at least some of the extraneous light.

The initial reading noted in Figure #10 attained a value that was not exclusively controlled by either the arsenate ion or sulfate ion, but seems to be due to a partially additive effect resulting when there is sufficient magnesium present to utilize all of the available sulfate and arsenate anions.

In general, the consistent competitive behavior of any two anions in combination with the magnesium appears to rest with the concentrations of the anions and relative stabilities of the compounds formed.

The variations in the flame emission intensities may possibly be best explained by three approaches. First, the formation of a stable intermediate compound, (as the pyro compound proposed by Baker & Johnson (1) and the tricalcium phosphate compound suggested by Leyton (8)), will explain the reduction in intensity values in that there would be a lesser number of magnesium oxide molecules available for excitation. In addition, this postulate is in agreement with the fact that molecular ratios appear to exist between the magnesium and depressant acid employed at the inflection point. However, this proposal does not seem to explain the increase in intensity observed when perchloric acid is in solution with the magnesium chloride.

Secondly, it may be proposed that the variations in intensities are
due to an increase or decrease in available energy due to the decomposition of acids or anions in the flame. If this decomposition adds to the available energy, more magnesium oxide could be excited, resulting in an enhancement as noted in the case of perchloric acid. Conversely, a depressant effect would be observed if the decomposition of the acid or anion absorbed energy. However, should this release or absorption of energy by the acid or anion be the sole operant, there should be no tendency to attain the stoichiometric relationships that have been suggested at the inflection point. Other investigators (1), (8), have noted ratios in flame photometry work with calcium emission.

A third approach in explaining variations in intensity may be that some of the excess acid forms gases that persist in the exterior portions of the flame. These gases could absorb or emit light of wave length essentially the same as the radiation being studied. This effect would be reflected as a decrease or increase in the intensity concentration relationship. However, since the variations in intensity are obtained from similar solutions for either wave length, this phenomenon, if present, is of more importance in the signal to background problems. It should be noted here that Lurie & Sherman (10), have determined by experiment and calculation that there exists a temperature difference of about $500^\circ$ K in favor of oxy-acetylene flame when compared to oxy-hydrogen flame. We can assume then that the data obtained and presented in this work were derived from a lower temperature when oxy-hydrogen flame was in use than when the oxy-acetylene flame was employed. As previously mentioned, the signal to background ratio was smaller when the oxy-acetylene flame was used as compared
to oxy-hydrogen flame. This factor determined the ultimate choice of oxy-
hydrogen flame for magnesium determinations, in spite of the fact that one
would expect more excitation of magnesium to occur in the higher tempera-
ture of the oxy-acetylene flame. The possibility of the existence of the
gaseous envelopes in the flame, the nature of which is dependent on the
flame source, should therefore not be overlooked.

Exploring these three suggested behaviors further, an attempt to ex-
plain the difference in the amount of depressant effect noted in the two
flames, may be made by returning to the formation of the stable intermed-
iate compound. Energy would be consumed in forming that intermediate, con-
sequently with either flame, the available energy for excitation would be
reduced. This would of course produce a lower intensity value. Removing
the energy necessary for the formation of this intermediate from the origi-
nal energy of either flame, would permit the originally higher temperature
of the oxy-acetylene flame (10), to excite more magnesium. Higher intensity
values would be maintained when a depressant acid is present in the mag-
nesium chloride solution. An alternate and essentially similar explanation
could be based upon the postulate that the intermediate compound formed is
so stable that there is considerable reduction in the number of magnesium
oxide molecules available and therefore excited in the flame. Leyton (8),
has proposed a degree of dissociation rather than a different type of
emission to explain the reduced emission.

The second postulate of absorption or emission of energy establishes
an interesting comparison when free energies of formation are considered.
A listing of the anions used in this investigation and arranged in the
order of their decreasing free energies of formation, (increasing stabil-
ities) show them to follow the order; perchlorate, nitrate, thiopride, ar-
senate, chromate, sulfate, and phosphate. The $\Delta_f^0$ values range from -10.7
kcal. for perchlorate ion to -241.0 kcal. for phosphate ion. This order is
noticeably consistent when these anions are arranged in order of their
ability to depress the intensity of magnesium emission, Figure #2. Although
these $\Delta_f^0$ values are for 25° C, the order might well be preserved to much
higher temperatures. The maximum temperatures determined by Lurie & Sherman
(10) for oxy-acetylene flame was 3410° K and 2933° K for oxy-hydrogen flame.
To arrive at a conclusion that absorption of energy upon decomposition of
the anions in the flame is related or consistent to their respective free
energies of formation, one should calculate the free energies of forma-
tion and the free energies for whatever reaction occurs within the flame at
the excitation temperature. There are factors however that restricts the
excitation temperature from reaching the maximum values of approximately
3000° K. The velocity of the solution through the aspirator, the bi-
products formed in the flame, the vapor pressures, the proportion of oxygen
to fuel and the nature of the burned and unburned gases in the flame all
would influence the actual excitation temperature. Thus free energy cal-
culation should add considerably to the understanding of what happens with-
in the flame, even though maximum flame temperatures were not used in the
calculations.

The absorption of energy would best explain the tendency, particularly
noted with chromic acid, for intensities to return to the original mag-
nesium standard value, after the inflection point had been reached. It has
been observed that other acids tend to return to the original intensity value of the standard, but only after the concentration of the acid was increased beyond the concentration limits presented in this work. It may well be that at those acid concentrations beyond the inflection point, another reaction occurs which is exothermic, and eventually provides sufficient energy to excite all of the magnesium.

It is reasonable to assume that not any one of the proposed behaviors is operating independently, but that a combination of two or all three contribute influence on the final behavior.

In order to further investigate flame photometry behaviors from a theoretical point of view, some knowledge of four situations would appear to be necessary. First, a more accurate knowledge of the actual operating flame temperatures. Second, more information into the composition of the compounds formed and their interaction within these temperature ranges. Third, what are the components in the flame at excitation, and what influence do they have in signal to background ratio? Fourth, what is the spectrum of each acid?
VIII. SUMMARY

In the flame photometry determination of magnesium, anionic effects are pronounced and must be accounted for in accurate quantitative measurements. Significant effects of phosphate, sulfate, arsenate and possible borate ions should be watched for their depressant action, whereas perchlorate ion will enhance the readings of the magnesium flame emission. Combinations of one or more anions in the magnesium system will be competitive and controlled by relative stabilities and concentrations of the anions.
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