

ANION EFFECTS IN EMISSION AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

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ABSTRACT

Many anions have a marked effect on the production of metal atoms in the flame. The mechanism of the emission-enhancing effect of anions is unknown in most cases. The effect of ClO_4^- , AlO_2^- , SO_4^{2-} anions on the determination of alkali, alkaline earth and transition metals was studied as a function of the excess of hydrogen and the flame profile measured under various experimental conditions. A difference was found between the atomic absorption and flame photometric results for transition metals. On the basis of the results, we tried to explain the mechanism of the effect of anions on the flame photometric and atomic absorption determination of metals.

INTRODUCTION

Various media, solid, liquid and gaseous, have been used for analytical purposes and it is difficult to decide which medium causes most problems in analytical chemistry. The answer to this question depends on the detailed knowledge of the medium used. Since analytical chemistry began, studies have been carried out mainly in aqueous media, so it is not surprising that the majority of data have been accumulated on reactions and interactions taking place in this medium. Fewer data are available on solid and gaseous media, in which analytical determinations are carried out also. In respect of the practical point of view of analytical chemists, the disturbing effects relating to the media can be eliminated by controlling the conditions of measurement experimentally. Empirical methods give possibilities for the determination of well-defined components under well-defined conditions. The problems of researchers who intend to develop a new analytical method are completely different, because it is possible only if the properties of the medium and its reactions are well-known. Here the effect of the medium cannot be overcome by speaking about matrix effect, which does not say anything about details.

Flame photometry and atomic absorption spectroscopy use gases of high temperature as a medium. The application of these techniques requires knowledge of the reactions taking place in the medium. The immense development of the theory of combustion processes in the last two decades has made it possible to understand most of the reactions in flames. In the

field of chemical reactions and chemical composition of flames, Semionov, Sugden, Alkemade, Gaydon and his co-workers, and others have done fundamental research. Most of the combustion reactions in hydrogen-oxygen and hydrogen-air flames have been clarified. To give explanations for reactions in hydrocarbon flames is more difficult. Not only the kinetics of numerous reactions but the intermediate products also are known in the former cases.

The flames used for analytical purposes can be laminar or turbulent. The hot gases of the flame can be separated from the air with shielding gases, as was worked out by West and his co-workers¹.

The compounds to be tested are introduced into the flame in various ways, among which atomization of the liquid can be used in practice. This is carried out with either the total consumption or the chamber-atomizer method. From knowledge of the parameters which affect the component introduced into the flame, it is obvious that both emission and absorption are further complicated by the atomization method employed. If a direct or total-consumption atomizer is used then the amount of solution entering the flame is influenced by its viscosity and surface tension. The effect of the latter depends on the deformation of the surface at the end of the capillary by the turbulent gas flow. It is also known that the aerosol issuing from the direct atomizer is polydispersed to a great extent. So the evaporation of the solvent takes place on various specific surfaces in the flame and it often happens that some drops go through the flame without total evaporation.

Chamber atomization offers better conditions over other methods in respect of dispersity. However, even when using this method other problems arise which affect the amount of aerosol in the flame.

The amount of solution atomized depends on the arrangement of the atomizer and the parameters of the solutions. So using a concentric atomizer the amount of liquid atomized is a complex function of the viscosity and the surface tension of the solution. *Table 1* shows results for this type of atomization, from which it can clearly be seen that the effect of surface tension is

Table 1. Time required for atomization of 0.33 ml of solution, referred to aqueous solutions as units at various alcohol concentrations, using direct atomization with a capillary 0.8 mm in diameter

Alcohol, %	Pressure of atomizing gas, atm				Rel. viscosity, (20°C)
	0.75	0.84	1.05	1.40	
0	1.00	1.00	1.00	1.00	1.00
5	0.82	0.86	1.09	1.13	—
10	0.83	0.85	1.10	1.28	1.53
20	1.00	1.10	1.30	1.61	2.17
30	1.18	1.23	1.47	1.96	2.70
40	—	1.27	1.69	2.24	2.90
50	1.30	1.30	1.75	2.32	2.86
60	—	1.31	1.83	2.32	2.66
70	—	1.18	1.68	2.20	2.36
80	1.08	1.00	1.55	2.03	2.00
90	—	0.77	1.35	1.76	1.60
100	0.61	0.61	0.97	1.29	1.18

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negligible, while that of viscosity is marked at high flowrates of the atomizing gas. If the directions of flow of the issuing gas and the atomized solution are not parallel, then the viscosity of the solution alone determines the atomization rate. This is presented in *Table 2*.

Table 2. Time required for atomization of 5.00 ml of solution, referred to aqueous solutions as units at various alcohol concentrations, using indirect atomization with a capillary 0.4 mm in diameter

Alcohol, %	Pressure of atomizing gas, atm									Rel. viscosity, (20°C)
	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
5	1.02	1.09	1.09	1.06	1.09	1.09	1.08	1.12	1.10	—
10	1.66	1.21	1.16	1.14	1.13	1.13	1.14	1.21	1.17	1.53
20	1.73	1.49	1.40	1.29	—	—	—	1.36	1.31	2.17
30	2.20	1.90	1.50	1.43	1.40	1.50	1.38	1.50	1.42	2.70
40	2.73	2.25	1.64	1.58	1.50	1.49	1.48	1.59	1.53	2.90
50	2.75	2.30	1.72	1.64	1.56	1.50	—	1.66	1.55	2.86
60	3.00	2.35	1.74	1.66	1.59	1.54	1.49	1.66	1.52	2.66
70	2.76	2.20	1.72	1.61	1.52	1.49	1.49	1.59	1.51	2.36
80	2.77	2.08	1.52	1.52	1.44	1.40	1.39	1.56	1.40	2.00
90	1.81	1.53	1.31	1.38	1.36	1.38	1.33	1.44	1.36	1.60
100	1.33	1.48	1.21	1.23	1.24	1.26	1.22	1.31	1.24	1.18

The aerosol in the chamber shows various coagulation reactions; this raises a very complex problem. Besides the flowrate of the gas, construction of the chamber etc., the ortho- and peri-kinetic coagulation is also controlled by the surface structure of the individual drops, which is affected by every component of the solution. Using a chamber atomizer only a small part of the solution atomized arrives at the flame. The proportion can be increased using an ultrasonic atomizer.

Considering the above facts, the question arises as to what kind of flame should be used for theoretical and practical studies. With regard to analysis, laminar flames with chamber atomizer have been covered, and applications of turbulent flames with direct atomizer have also been found in the literature.

The question is more interesting where theoretical investigations are concerned. The laminar flame has a well-defined combustion zone in space. This is especially true if a shielding gas is used because the diffusion after-burning around the periphery of the flame is eliminated. The reactions and equilibria taking place in hydrogen flames have been clarified by many researchers. First of all, the equilibria and kinetics of the OH and H radicals were studied in detail. The temperature profile of such flames is known, and an example is shown in *Figure 1* after Zeegers and Alkemade². A temperature maximum can be seen above the combustion zone.

The recombination reactions of H and OH radicals were investigated by numerous researchers and it was shown that the concentration of the two components, which quickly come into equilibrium with each other, decreases with the height of the flame. This is presented for H radicals in *Figure 2*. The mechanism of the recombination reaction has been clarified^{3,4}. Although

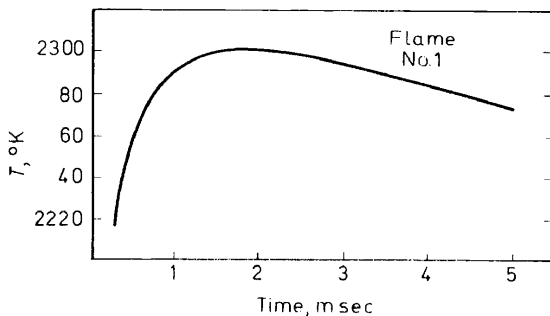


Figure 1. Temperature profile of acetylene-air flame (1.68:20:6) after Zeegers and Alkemade².

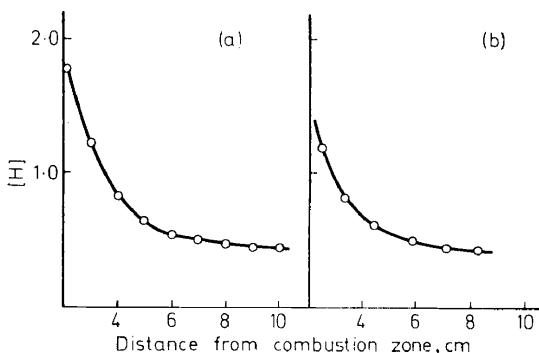


Figure 2. Values of H radical concentration at various heights in the flame: (a) measured by the CuH band emission, (b) by the Li-Na method.

hydrocarbon flames are complicated, even so many reactions and equilibria have already been elucidated⁵⁻⁸.

In spite of the fact that there are still numerous unresolved questions in the field of laminar flames, their application is already accepted for theoretical investigations. However, while agreeing that laminar flames with chamber atomizers are in some ways more suitable for analytical purposes than the noisy turbulent flame with a direct atomizer, I still cannot agree completely with this view. I still prefer the turbulent flame with direct atomizer for theoretical studies, since here the overall reaction is not complicated by the coagulation of the aerosol.

The coagulation reactions of aerosols have been studied by colloid chemists and it has been stated that besides the number of particles, the surface structure of the droplets also plays an important role in coagulation. Our studies on aerosol coagulation support the results found in the literature, from which it can be concluded that the application of a chamber atomizer seems to be very complicated for theoretical studies, although the degree of dispersion of the aerosol is in a narrow range. To avoid misunderstanding, I would like to re-iterate that there are also many unresolved problems with total consumption burners. The degree of dispersion of the

droplets in a flame varies over a wide range and so droplets can pass through the flame without total evaporation. This may be prevented by using fast turbulent gas flow and narrow capillaries for atomization. In this case, the emission intensity in the flame is a function of the solution atomized and it does not depend on the surface tension of the solution. This indicates that the total amount of the component introduced into the flame takes part in every consecutive reaction.

For theoretical investigations a turbulent flame with direct atomizer can be used successfully, in my opinion, and my co-workers and I often use

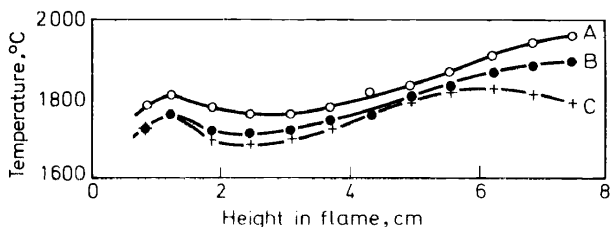


Figure 3. Flame temperature profile in the hydrogen-air flame at various hydrogen flowrates: (A) 750; (B) 650; (C) 540 l/h. Air flowrate: 170 l/h. Solution of NaCl sprayed into flame.

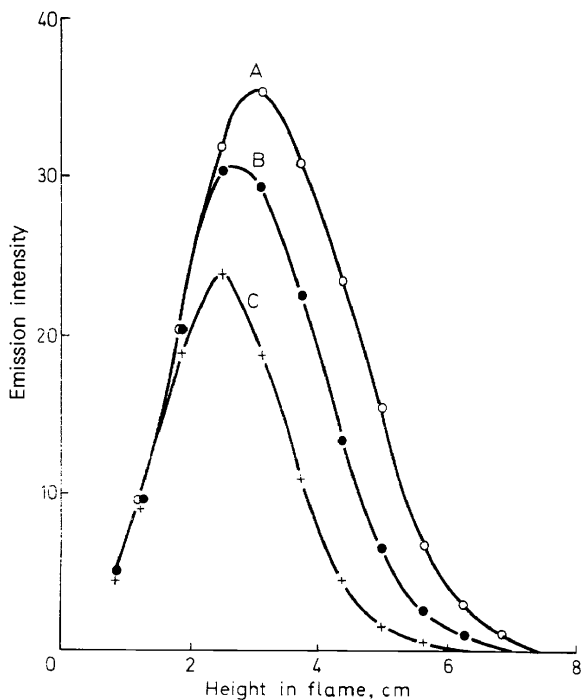


Figure 4. Flame emission profile by CuH in the hydrogen-air flame at various hydrogen flowrates: (A) 750; (B) 650; (C) 540 l/h. Air flowrate: 225 l/h. Solution 10^{-2} M Cu^{2+} , Wavelength: 4290 Å. Slit width: 0.2 mm.

this type of flame. For a true understanding of the various reactions, primarily the anion effect which will be discussed in more detail later, it is necessary to study the various parameters of turbulent flames. I carried out this sort of work with my co-worker, Dr Halls.

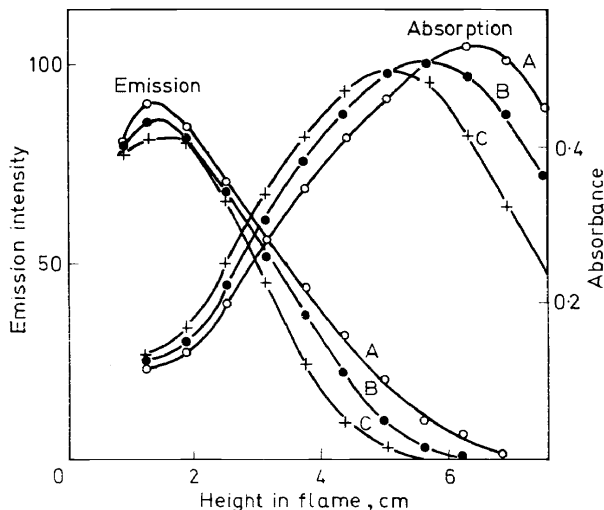


Figure 5. Flame emission profiles of excited OH radicals and of absorption by ground-state OH radicals in the hydrogen-air flame at various hydrogen flowrates: (A) 750; (B) 650; (C) 540 l/h. Air flowrate 225 l/h. H₂O sprayed into flame. Wavelength 3094 Å. Absorption source: Ni lamp; current 25 mA; slit width 0.05 mm. Emission slit width: 0.2 mm.

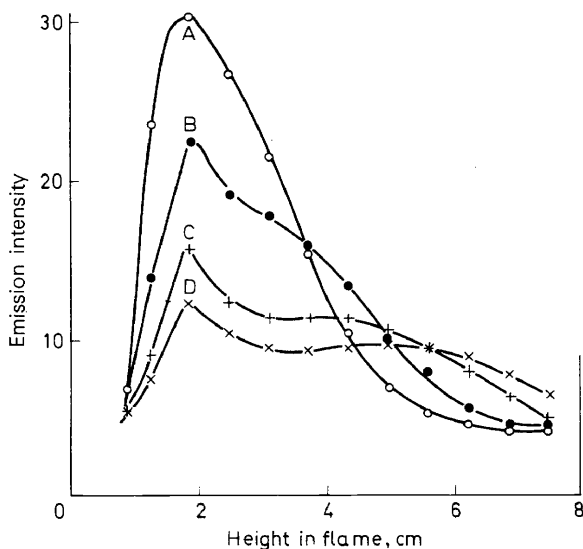


Figure 6. Blue continuum flame profile in the hydrogen-oxygen flame at various hydrogen flowrates: (A) 410; (B) 540; (C) 650; (D) 750 l/h. Oxygen flowrate: 125 l/h. H₂O sprayed into flame. Wavelength 4700 Å. Slit width: 0.2 mm.

Among the parameters of turbulent flames, the most important is the temperature profile. Some typical results using a hydrogen-air flame⁹ are shown in *Figure 3*. From this, it can be seen that the temperature is practically constant over a wide range of flames. However, in a hydrogen-oxygen flame a temperature maximum is observed.

It can also be shown that an equilibrium between H and OH radicals can be established in a turbulent flame, in spite of enlargement of the combustion zone. The concentration profiles of H and OH radicals shown in *Figures 4* and *5* are quite different from those of laminar flames. From the latter the shape of the blue continuum results, as presented in *Figure 6*. According to Padley, the blue continuum is produced by direct recombination of H and OH radicals, as proved by our results.

MOST IMPORTANT REFERENCES CONCERNING THE ANION EFFECT IN FLAME SPECTROMETRY

The most difficult problem of flame spectrometry, the anion effect, will be discussed below. This problem of the anion effect was introduced by Huld¹⁰ from a theoretical point of view. However, even before this Török had tried out the anion effect for analytical purposes, using it in titration of phosphate with calcium and employing a flame emission technique.

Huld studied the effect of aluminium on the emission of calcium and found that aluminium nitrate caused a greater decrease in calcium emission than did aluminium chloride. This was explained as by compound formation in the flame. At the same time, it was also stated that the emission spectrum of an assumed calcium-aluminium compound was not obtained. Since then, the literature on the effect of aluminium has been increasing without a final conclusion being drawn.

To explain the anion effect, the paper of Margoshes and Vallee¹¹ gave a new basis. These authors introduced various metal salts into the flame on a wolfram wire, and from the metal emission conclusions were drawn regarding the evaporation rate. Furthermore, they stated that the evaporation rate is of great importance in the flames studied. On the basis of their results, it can be imagined that compounds of high melting-point can pass through the flame without evaporation. This agrees with the hypothesis of Schuhknecht and Schinkel¹², who sought to interpret the anion effect in terms of the evaporation rate of particles.

Alkemade and his co-workers¹³⁻¹⁶ used these studies as a basis for explaining the effect of such anions as sulphate, phosphate and aluminate. They supposed that compounds were formed of the alkaline-earth metals with the above-mentioned anions, which form particles of low evaporation rate. Alternatively, if the metal component studied is in such a solution in which particles of low evaporation rate can also be formed and they occlude the component measured, then an emission decrease will also be observed. These two basic cases are found when a calcium solution is atomized in the presence of aluminium chloride (AlCl_3) or aluminium nitrate $\{\text{Al}(\text{NO}_3)_3\}$. If $\text{Al}(\text{NO}_3)_3$ is used then the emission can fall to zero, because the calcium salt is occluded in the highly refractory particles.

Alkemade also explains the increase of emission effect of a third component

also for both the cases discussed previously. The third component can act through the elimination of the component of low evaporation rate, or in the case of occlusion, it acts by increasing the degree of dispersion of the aerosol. To exclude assuming that the anion effect is caused by the reactions in the homogeneous phase, the metal and the anion were atomized separately into the flame. In this case no anion effect was observed.

About 1956, Fischer and Doiwa¹⁷ went back to the Huldtt concept. According to them, the anion effect on calcium was caused by formation of the thermally stable calcium aluminate vapour.

Since then, numerous papers have been published, some in favour of Alkemade's assumption, some against, and others inconclusive.

Winefordner and his co-workers¹⁸ pointed out from light-scattering studies that if a large amount of aluminium was atomized, then solid particles were found in the upper part of the flame when using either a pre-mixed burner or a direct atomizer burner.

According to Shaevich¹⁹, the sulphate ion hinders only the evaporation rate of the particles, while phosphate gives a combined effect. Poluektov²⁰ nearly comes to the same conclusion and interprets the sulphate effect in terms of evaporation of the particles. Furthermore, he points out that potassium emission decreases even if the potassium and phosphate are atomized separately. The phenomenon is interpreted as the formation of stable potassium phosphate compound in the flame.

For interpretation of the aluminium effect Rubeska and Moldan²¹ also accepted the concept of aerosol evaporation. However, they found that the releasing effect of aluminium occurs only if lanthanum chloride and oxine or EDTA are added. In their opinion, the components partly hinder hydrolysis of the alkaline-earth salts and partly the reaction of aluminium oxide.

Adams and Passmore²² pointed out that these compounds do not give a similar releasing effect with sulphate or phosphate.

Smith and Winefordner²³ emphasize that the influence of phosphate on calcium is caused by the slow evaporation of calcium phosphate using a direct atomizer burner. On the other hand, they observed that the phosphate interferes in the calcium determination only at higher concentrations using a laminar flame and supposed that the ortho- and pyro-phosphate transformation also plays a role in this respect.

Accepting Alkemade's idea, Dinnin²⁴ goes further and underlines the importance of the pre-reactions in aqueous solutions. This was proved by experiments concerning the releasing effect. However, studies on the releasing effects led to further complications. Yofé and Finkelstein²⁵ suggested the use of iron salts to release the phosphate effect on calcium. Studying this reaction von Schouwenburg and van der Wey²⁶ came to the conclusion that some sort of Ca-Fe compounds should exist in the flame, since a very small amount of iron markedly decreases the effect of phosphate.

The anion-interference effect only changes quantitatively with the flame temperature; this was pointed out by Smith, Stafford and Winefordner²⁷.

The atomic absorption method has added markedly to knowledge of the anion effect studied with emission flame spectroscopy. Allan²⁸ dealt first with the problem of the anion effect in atomic absorption and gave results on the interference of aluminium, phosphate and sulphate on the

absorption of magnesium. David²⁹ then stated that the anion effect is a function of the absolute concentration of metals. Leithe and Hofer³⁰ reported on the fact that absorption of magnesium is not affected either by sulphate or phosphate in an acetylene-air flame. Halls and Townshend³¹ accepted the sublimation theory of the particles as explanation of the diminishing emission effect of SO_4^{2-} , PO_4^{3-} and COO_2^- , and extended it with the mechanism of the reaction between solid magnesium oxide particles and H radicals, which produces magnesium atoms. They also studied the effect of aluminium on magnesium, and the anion-interference effect was attributed to the formation of mixed oxides. Furthermore, they showed that sulphate and nitrate increase the effect of aluminium to a great extent. This phenomenon was also interpreted in terms of the formation of mixed oxides.

From further studies on the anion-interference effect Rocchiccioli and Townshend³² concluded that according to Alkemade, the evaporation rate of the solid particles explains the influence of metal concentration on the degree of the anion-interference effect. In low metal concentrations, particles of great degree of dispersion are formed and so the reaction with hydrogen radicals mentioned previously takes place on larger specific surfaces and the reaction tends to completion.

Veenendaal and Polak³³ stated that phosphate increases the atomic absorption of thallium in contrast to the effect of phosphate observed in flame emission photometry. A large excess of sodium or potassium can release this effect completely.

Sachdev, Robinson and West³⁴ pointed out the enhancing effect of aluminium on the absorption of vanadium in an acetylene-nitrous oxide flame. The absorption follows a saturation curve. Saturation is reached at 2:1 ratio of aluminium to vanadium. The same effect was also found for titanium. The authors explain this effect in terms of the formation of very stable metal oxides, which help to produce atomic vanadium in the flame.

Amos and Willis³⁵ show that beryllium absorption is not influenced by phosphate or sulphate. Aluminium causes a small absorption-decreasing effect on beryllium in higher concentrations only. The comparison made between the results obtained in acetylene-nitrous oxide and acetylene-air flames is very important. It has been pointed out that the change in atomic absorption of magnesium is similar to that of its emission in an acetylene-air flame. However, in an acetylene-nitrous oxide flame the emission increased as a function of aluminium concentration. A similar phenomenon was found for the phosphate effect on calcium in both flames.

Slavin and his co-workers³⁶ found similar results for calcium and barium. The effect of phosphate on these metals is negligible in acetylene-nitrous oxide flames but marked in acetylene-oxygen flames.

Furthermore, Willis³⁷ reports that the absorption of calcium and magnesium is not influenced even by 100 times excess of phosphate or 1000 times excess of aluminate in an acetylene-nitrous oxide flame.

Harrison and Wadlin³⁸ state that the decreasing effect of aluminium on magnesium absorption varies as a function of height in an acetylene-air flame, and it stops at about 2 to 3 cm high, above which an absorption-increasing effect can be observed.

If an acetylene-nitrous oxide flame is used, then aluminium has an

absorption-decreasing effect in the vicinity of the tip of the burner. Furthermore, they observed that the atomic absorption of magnesium increases in an acetylene-air flame if the flame becomes more reducing in character. Under the same conditions, the negative effect of aluminium increases, while in acetylene-nitrous oxide flames, the same effects were not observed.

The papers discussed above involve only the most important results of anion effects in flame spectrometry. It was not my intention to deal with papers concerning analytical methods based on anion effects or their elimination. It is obvious that the literature discussed so far offers a wide

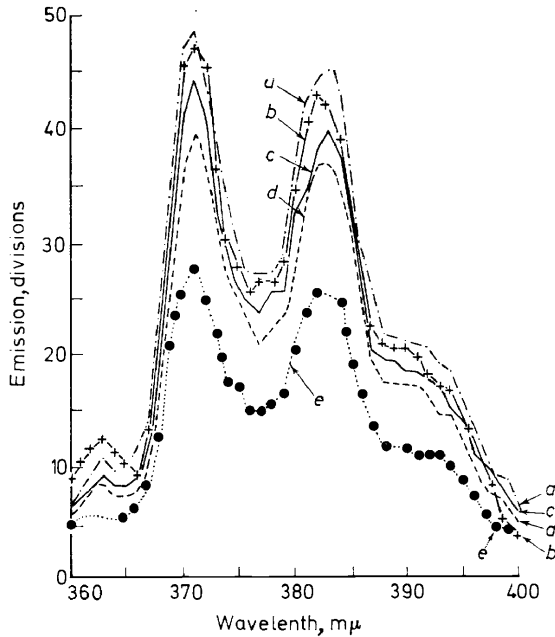


Figure 7. Emission of various salts of 5×10^{-2} M magnesium: (a) in a solution of 50% ethanol, (b) in a solution of 1 M HClO_4 , (c) in a solution of 1 M NH_4OH and 1 M NH_4Cl , (d) in a solution of 1 M HNO_3 , (e) in a solution of 5×10^{-2} M acetate.

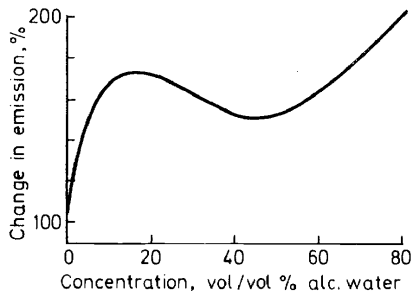


Figure 8. Change in emission intensity of Mg in solution of ethanol-water in the presence of 1 M HClO_4 .

variation of the phenomena concerning the anion effect. Unfortunately, to compare the results of various papers is difficult or impossible because authors generally do not give details about the most important parameters of flames.

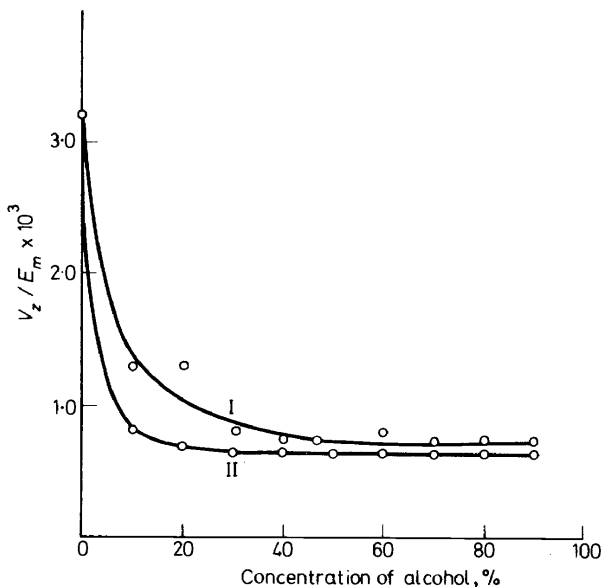


Figure 9. Reciprocal value of emission of Mg corrected for viscosity of ethanol-water solutions. (I) Ethanol-water; (II) Ethanol-water containing M HClO_4 .

In discussing the literature, the effect of aluminium, sulphate and phosphate was the main concern, and the effect of other anions has not been summarized. Before presenting our results and discussing further the anion effect, I would like to point out that the concept of the anion effect is a relative one; it relates to the salts which can most easily be used chemically or obtained commercially. Since these salts are frequently chlorides, the anion effect is referred to them. In my opinion, reference to chlorides can be accepted in the case of alkali metals because they may enter directly, without hydrolysis, into a thermal decomposition reaction. The problem is not so simple with alkaline-earth metals. As Figure 7 shows³⁹, the magnesia mixture gives the highest emission if the alcoholic solutions or solutions containing perchloric acid are not considered. From Figure 7 it can clearly be seen that the perchlorate increases the emission of the metals; this is attributed to the energy released on decomposition of perchloric acid. That this reaction is not simple is shown by Figures 8 and 9, where the examination of magnesium is presented in alcoholic medium and solutions containing perchlorate and alcohol. According to the results, the effect of the perchloric acid is mainly due to the change in the viscosity of the solution. Wänninen and Lindholm⁴⁰ also suggest the use of solutions containing perchloric acids in atomic absorption spectroscopy.

DISCUSSION OF THE EFFECT OF SULPHATE, PHOSPHATE AND ALUMINIUM ON THE BASIS OF OUR RESULTS

As pointed out above, our experiments were carried out with a turbulent flame and direct atomizer thus eliminating the problems of coagulation of the aerosol.

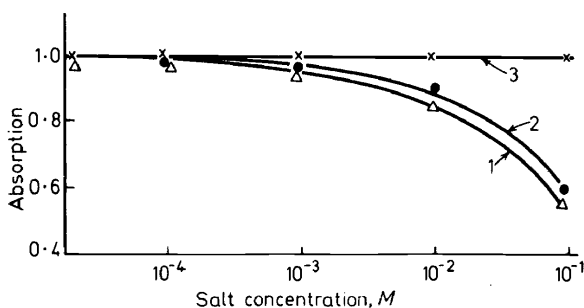


Figure 10. Effect of anion on absorption of 10^{-2} M sodium. Height in the flame: 3 cm. Wavelength: 5896 Å. 1, $(\text{NH}_4)_2\text{SO}_4$; 2, K_2SO_4 ; 3, NH_4OH .

Table 3. Change in emission of sodium in the presence of various anions

Interfering material		Change in the emission (%) at various NaCl concentrations, M		
Formula	Conc., M	10^{-4}	5×10^{-4}	5×10^{-3}
HCl	0.1	0.0	+1.13	0.0
H_2SO_4	0.1	0.0	+0.32	0.0
HClO_4	0.1	+23.5	+4.85	0.0
$\text{H}_2\text{C}_2\text{O}_4$	0.02	0.0	+0.32	-0.42
NH_4OH	0.1	0.0	+0.32	0.0
$(\text{NH}_4)_2\text{SO}_4$	0.1	-11.8	-8.6	-6.35
$(\text{NH}_4)_3\text{PO}_4$	0.1	-5.9	-6.15	-4.15
$(\text{NH}_4)_2\text{C}_2\text{O}_4$	0.02	0.0	+0.32	0.0

Table 4. Change in emission of lithium in the presence of various anions

Interfering material		Change in emission (%) at various LiCl concentrations, M		
Formula	Conc., M	10^{-4}	5×10^{-4}	5×10^{-3}
HCl	0.1	0.0	+0.2	0.0
H_2SO_4	0.1	-8.9	-4.25	-3.12
H_3PO_4	0.1	-11.1	-4.5	-3.7
$\text{H}_2\text{C}_2\text{O}_4$	0.02	-7.8	+0.2	-0.45
NH_4OH	0.1	-8.9	-0.94	-0.45
$(\text{NH}_4)_2\text{SO}_4$	0.1	-22.2	-14.8	-10.8
$(\text{NH}_4)_3\text{PO}_4$	0.1	-21.0	-10.6	-9.2
$(\text{NH}_4)_2\text{C}_2\text{O}_4$	0.02	-5.55	-1.2	+0.45

Our earliest results concerning the emission of lithium and sodium show that the same amounts of ammonium sulphate and ammonium phosphate

decrease the emission of the alkali metals to a greater extent than the corresponding acids (*Figure 10, Tables 3 and 4*). The reason for this phenomenon was attributed to thermal dissociation of the salts and it was supposed that if salts contained more than one alkali atom, then further dissociation of the metal is hindered.

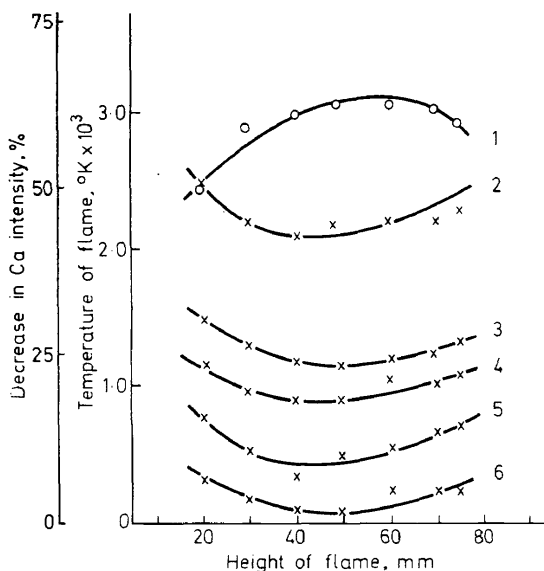


Figure 11. Decrease in Ca-intensity as a function of height in flame and flame temperature of a hydrogen-oxygen flame. 1—Flame temperature. [Ca]:[Al] = 2—1:5, 3—1:2, 4—1:1, 5—1:0.3 and 6—1:0.1.

Experiments were carried out to examine the effect of aluminium, phosphate and sulphate on calcium. The changes caused by aluminium in the emission of calcium measured as a function of height in flame are presented in *Figure 11*. *Figure 11* also contains the temperature profile of the hydrogen-oxygen flame, and it can be seen that the depressive effect of the aluminium changes as a function of the flame temperature. It was proved by calculation that the thermal dissociation of the calcium aluminate $\{Ca(AlO_2)_2\}$ compound determines the calcium emission in the flame⁴¹.

If the ratio of hydrogen and oxygen is varied in the flame, then not only the flame temperature but the ratio of the various components in the flame will also be changed. It was found that if the ratio of hydrogen to oxygen is increased, then the degree of the interference effect of aluminium is decreased, in spite of the fact that the temperature of the flame decreases. The excess hydrogen shifts the reaction between H and OH radicals towards the formation of H_2O and H radicals.

The effect of sulphate and phosphate was studied as a function of the flame composition and height in flame. These results are presented in *Figures 12 to 14*. It is obvious that, in agreement with the literature, the

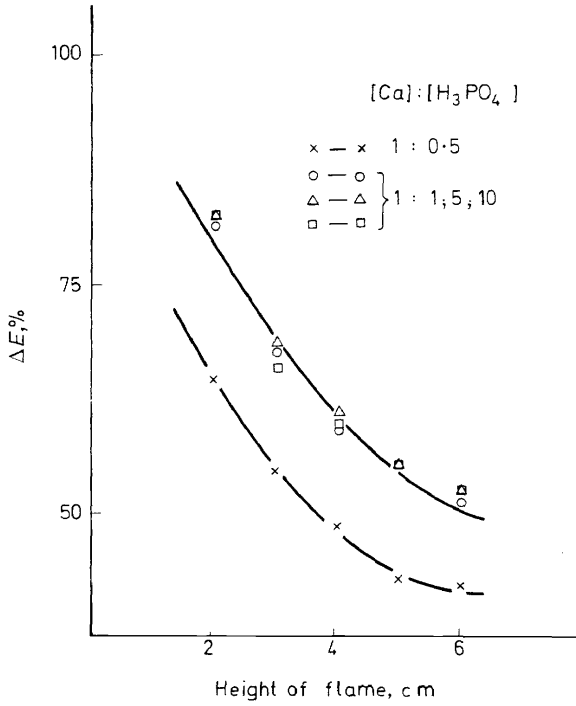


Figure 12. Effect of PO_4^{3-} as a function of flame height on emission of Ca.

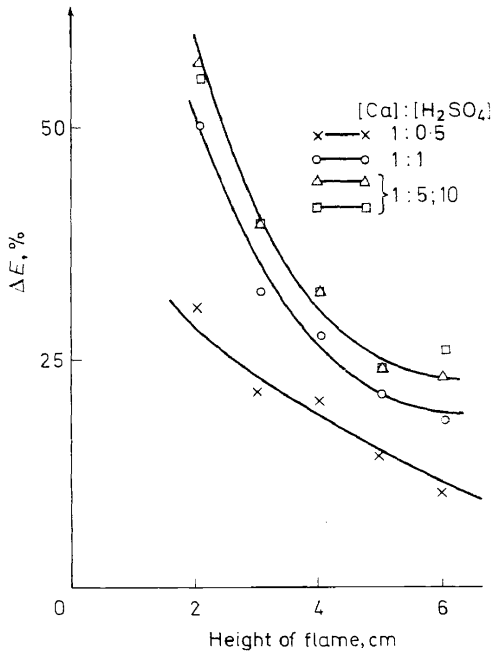


Figure 13. Effect of SO_4^{2-} as a function of flame height on emission of Ca.

emission-depressive effect decreases with height in flame. On the other hand, if the composition of the flame is shifted towards an oxidizing character, the correlations are not so simple.

The effect of aluminium, sulphate and phosphate anions in flames of the same composition is summarized in *Figure 15*.

Our examinations were also extended to transition metals and it was

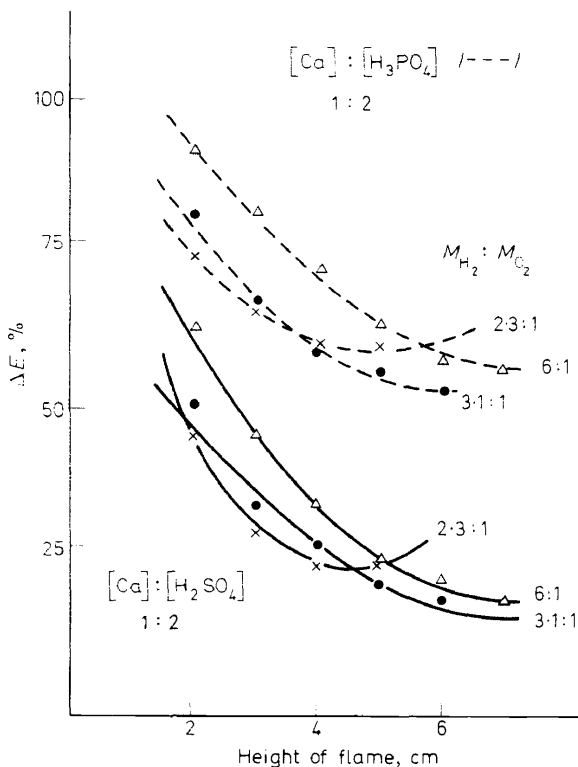


Figure 14. Effect of SO_4^{2-} and PO_4^{3-} anions as a function of flame composition and height in flame on emission of Ca.

shown that aluminium, for example, increases the absorption of copper. The absorption and emission profiles of cobalt were determined in the presence of sulphate and this is shown in *Figures 16* and *17*. During the examinations 10^{-2} M CoCl_2 and 10^{-1} M H_2SO_4 were used. From the figures it can be seen that the emission and absorption maxima are not at the same height in the flame, but their position is not influenced by sulphuric acid. In *Figures 18* and *19* the effect of the three disturbing anions is presented as a function of interfering anion concentration. The interference effect of aluminium is more marked in emission than in absorption, which is generally true for the transition metals.

A more interesting effect appears with iron. Here, the aluminium increases the emission, while it decreases the absorption. The effect of sulphate and

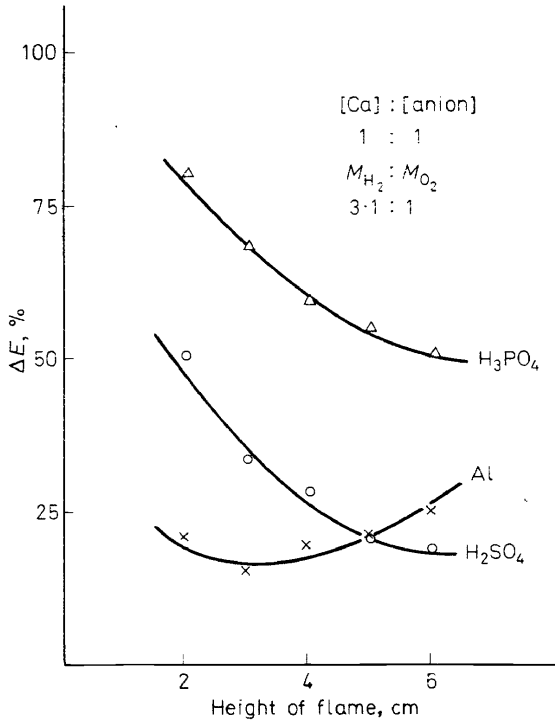


Figure 15. Effect of Al^{3+} , SO_4^{2-} and PO_4^{3-} at the same flame composition and at the same Ca/anion ratio.

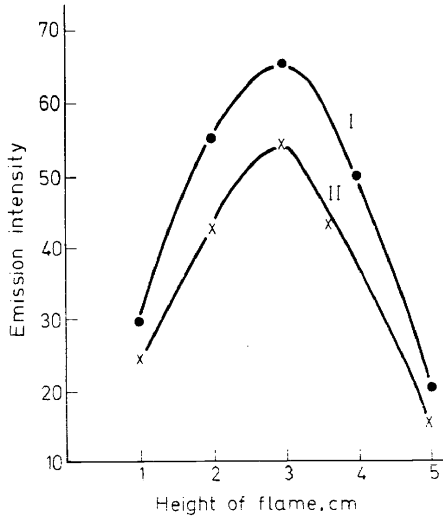


Figure 16. Flame profiles of emission of 10^{-2} M cobalt in the absence (I) and in the presence (II) of 10^{-1} M H_2SO_4 , respectively. Wavelength 3580 Å, slit width 0.1 mm.

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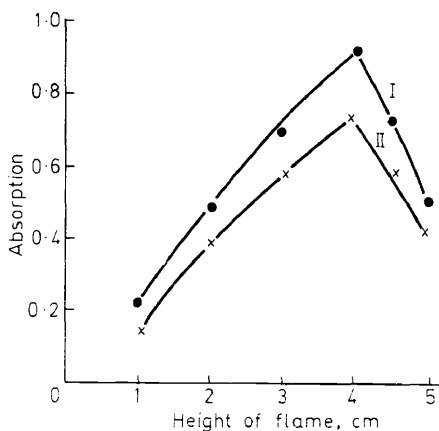


Figure 17. Flame profiles of absorption of 10^{-2} M cobalt in the absence (I) and in the presence (II) of 10^{-1} M H_2SO_4 , respectively. Wavelength: 2412 Å, slit width 0.05 mm.

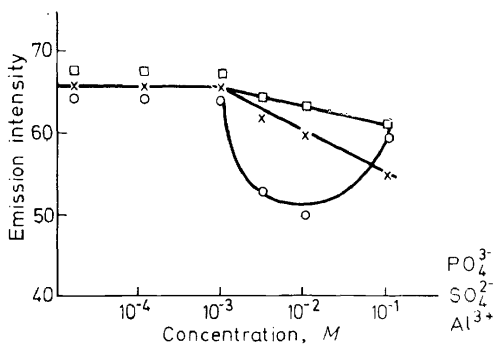


Figure 18. Anion effects on emission of 10^{-2} M cobalt. Wavelength: 3580 Å, slit width 0.2 mm. Height of flame: 3 cm. \square Al^{3+} , \times SO_4^{2-} , \circ PO_4^{3-} .

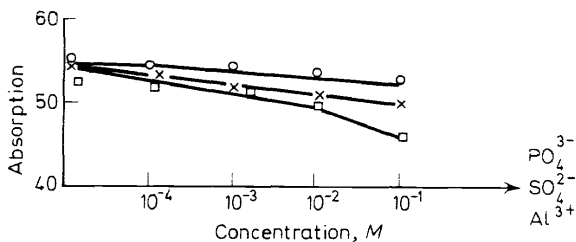


Figure 19. Anion effects on absorption of 10^{-2} M cobalt. Wavelength: 2410 Å, slit width 0.05 mm. Height in flame: 3 cm. \square PO_4^{3-} , \times SO_4^{2-} , \circ Al^{3+} .

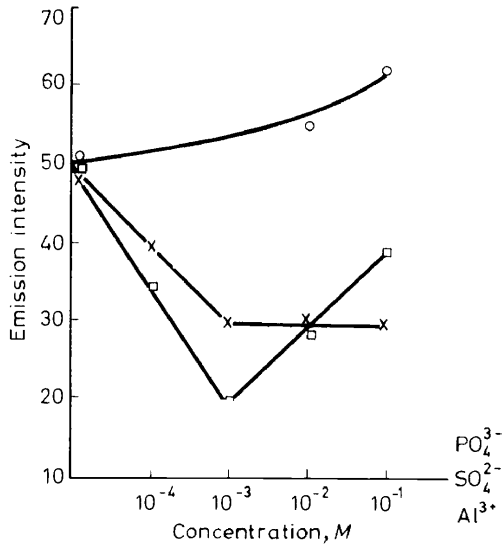


Figure 20. Anion effects on emission of 10^{-2} M iron. Wavelength: 3720 Å, slit width: 0.17 mm. Height in flame: 3 cm. □ PO_4^{3-} , × SO_4^{2-} , ○ Al^{3+} .

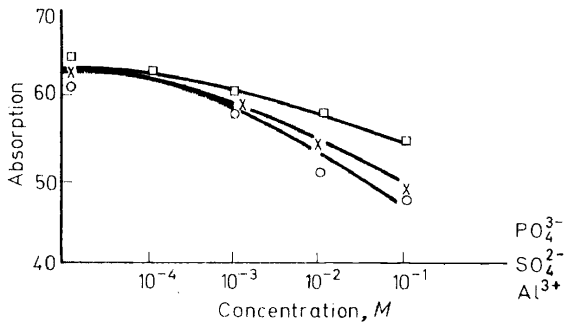


Figure 21. Anion effects on absorption of 10^{-2} M iron. Wavelength: 2488 Å, slit width: 0.13 mm. Height in flame: 3 cm. □ Al^{3+} , × SO_4^{2-} , ○ PO_4^{3-} .

phosphate is greater in emission than absorption as shown in *Figures 20 and 21*.

The results presented so far do not prove that Alkemade's model concerning the anion effect can describe the phenomenon completely. Similarly, the results of Amos and Willis, Slavin *et al.*, Willis, and Harrison and Wadlin do not agree with this. If the evaporation effect is controlling, then the interference effect should exist in acetylene-air, acetylene-oxygen and acetylene-nitrous oxide flames also. However, these results prove clearly that it is not the temperature but the composition of the flame which plays an important role in the anion effect.

Our experiments reported above for the effect of aluminium on the

emission and absorption of calcium at various flame compositions also prove this.

According to our work, the effect of aluminium can only be understood in relation to thermal equilibrium in the flame. This cannot be said so definitely for sulphate and phosphate. However, according to Halls and Pungor⁹, the concentration of H_2O reaches high values (*Figure 22*) in the upper part of the flame, and it can be expected that the hydrolysis will be

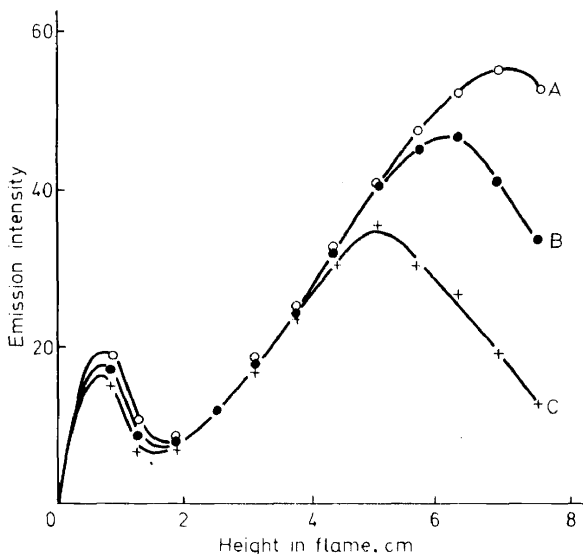


Figure 22. Flame profile of emission from H_2O molecules in the hydrogen-air flame at various hydrogen flowrates: (A) 750; (B) 650; (C) 540 l./h. Air flowrate 185 l./h. H_2O sprayed into flame. Wavelength: 9500 \AA , slit width: 0.2 mm.

shifted toward completeness in this region. Thus, it is understandable that the anion atomized separately has no, or very little, effect on emission and absorption of the metal. Furthermore, the polymerization of these anions may also be considered in this respect.

The great difference obtained for the transition metals in emission and absorption spectroscopy can be explained by the assumption that the decrease in the emission is probably due to the loss of the energy of the excited atom through collision with the anion of many degrees of freedom. The enhancing effect of aluminium on the absorption of various transition metals can be understood by the formation of aluminium oxides more stable than the transition metal oxides.

However, I should not like anyone to conclude from the foregoing discussion that I underestimated the effect of evaporation of the aerosol. I say that it has an emphasized effect in respect of the overall picture of the flame at low heights. The evaporation of the aerosol is a slow reaction as shown in *Figure 23*. From this, it can be seen that the number of H_2O particles measured on the basis of light scattering disappears in the lower part of the flame when using a suitable atomization rate. I believe that the

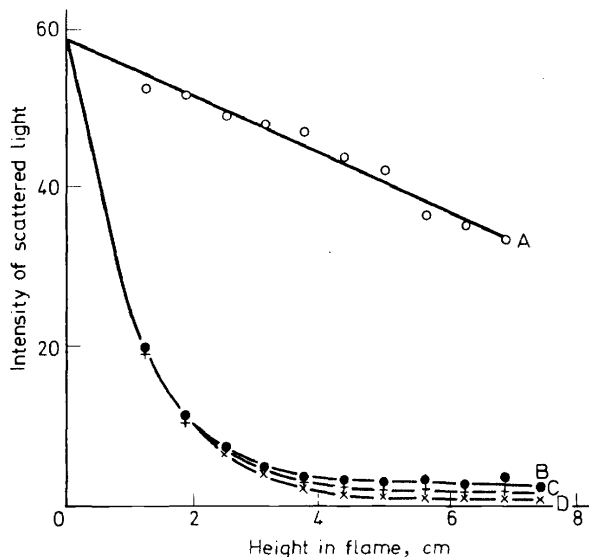


Figure 23. Extent of evaporation of water in a hydrogen-air flame as determined by light scattering. (A) Amount of light scattered in absence of flame (air only going through the burner) (B) to (D): amount of light scattered in presence of flames. Air flowrate: 225 l/h. Hydrogen flowrates: (B) 540; (C) 650; (D) 750 l/h. Wavelength: 5000 Å, slit width: 0.3 mm.

rate of evaporation and the equilibria and kinetic reactions of the components, being far from equilibrium, together determine the anion effect.

Finally, I would like to suggest direct measurement for the evaporation and sublimation rates of aerosols using the method of Hieftje and Malmstadt⁴⁴ which was worked out for drop-generation. On this basis, a final interpretation of the evaporation effects in flame spectrometry may be given. In the knowledge of the latter and by considering the anion effects discussed previously, a complete theory of anion effect may possibly be worked but in the near future.

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