

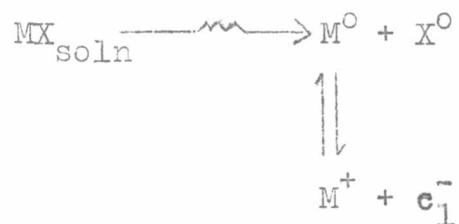
CHAPTER V



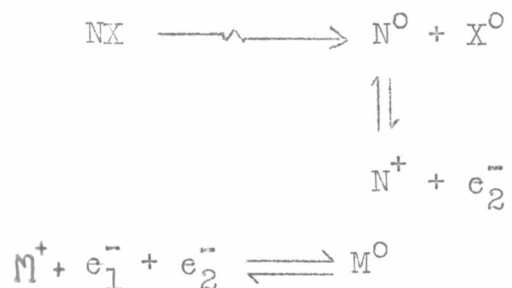
DISCUSSION AND CONCLUSION

When solutions of alkali metals are introduced into the flame, ionization and compound formation are likely to occur. From equation (23) and (27) the extent to which ionization and compound formation occurs depends on the values of K_p and $K_i(T)$ which in turn depends on the ionization potential and heat of dissociation respectively of alkali metal compounds formed. Table III shows the degree of ionization which depends on the ionization potential of alkali metals; the order is $Cs > Rb > K > Na > Li$. The values are of sufficiently low energy that at flame temperatures a significant amount of the metal supplied will be ionized, lowering the concentration of ground state metal atoms in the flame. The percentage ionization will be least for Li and greatest for Cs.

The ionization of alkali metal (M) in the flame is represented by the following equation



If another alkali metal (N) which has lower ionization potential is introduced the partial pressure of the electrons in the flame displaces the ionization equilibrium and partial pressure of ground state atoms of M is increased. The displacement in equilibrium is governed by the law of mass action, and can be represented as follows



The concentration of M° is dependent partially on the electron concentration present. This electron concentration in turn depends on the ionization potential of alkali metals (M,N) used. In case when N has much lower ionization potential than M, the electron concentration is increased to a greater extent and

hence will shift the equilibrium in favor of the atom production of M.

Considering compound formation, when the chloride salts of alkali metals are introduced into the flame it is possible that not only hydroxide and oxide that are formed but also the chloride themselves, as is evident from the D_0^0 values for chlorides in Table II. In the case of the chloride it should be borne in mind that the chloride concentration is probably of the same magnitude as OH, H or O in the flame and that it is unlikely to play a major part in compound formation, as HCl and Cl₂ are relatively stable alternatives for Cl.

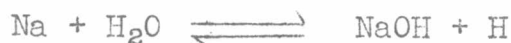
For alkali hydroxides the work of Sugden and his collaborators (17) has showed that in fuel rich H₂ + N₂ + O₂ flames the alkali metals form hydroxides mainly according to the equilibrium



The value of equilibrium constant K are such that for Li and Cs, and to a lesser extent Rb, Na and K, a considerable proportion of the added metal is present



in the flame gases in the form of hydroxide. LiOH has the highest dissociation energy and is by far the most stable. Changes in $[H]$ will effect the production of LiOH and hence the atomic metal concentration. Although radical populations may differ somewhat the same processes are likely to occur in C_2H_2 - air flames. In the case of Na, as well as hydroxide formation, there is evidence of the superoxide forming in fuel lean flames. McEwan and Phillips (18) observed its presence by means of emission continuum when a strong solution of a Na salt is atomized into the flame which was attributed to NaO_2 . This spectral evidence has yet to be identified positively. They proposed that in hydrogen rich flames, the concentration of atomic Na is governed by the equilibrium



In the presence of chlorine, the reaction



is also feasible. In the oxygen - rich flame, the reaction



is expected. (where M is any third body). The dissociation energy $D_{\text{Na-O}_2}^{\circ}$ has been calculated as $65.3 \text{ kcal mol}^{-1}$ at flame temperature 2000°K . In the system studied the temperature is higher and D_0° value is such that it is considered to be unstable in the flame. Hence the existence of NaO_2 can be negligible .

For K and Rb hydroxides, values of D_0° are very close together and slightly greater than that of Na. This shows that their stability lies somewhat near that of Na but in fuel lean flame McEwan and Phillips noted that there is evidence for KO_2 and its stability is greater than that of NaO_2 . Table II shows that the D_0° for CsOH is second to LiOH in magnitude, CsOH should be formed in the flame in significant amounts.

Another factor which may govern these interference phenomena is the concentration of reactive flame species which differs between flames. It can be seen roughly from Table I that for fuel lean flame $[\text{OH}] > [\text{O}] > [\text{H}]$ then the formation of oxides is likely providing oxides are stable at flame temperatures.

Hydrides are not sufficiently stable to be considered. In fuel rich flames $[[\text{OH}] > [\text{H}] \gg [\text{O}]]$ the order is reversed. As it has been mentioned previously, this has to be considered together with the value of D_{O}^{O} , the dissociation energy of the compound.

From the result of Li it is seen that the effect of increasing the absorption due to the addition of another alkali metals is very small in magnitude compared to the other systems studied. This is because Li itself is less highly ionized in the flame and a large percentage of the Li is present in the form of ground state atoms already. Secondly, since the hydroxide of Li is more stable than any other the competition for OH from an alternate hydroxide forming is small. Upon the addition of another more readily ionizable metal, although the electron concentration is increased shifting the ionization reaction of Li in the direction of Li atom production, it will not influence the absorbance of Li greatly as ionization is initially very small. After this no matter how much the electron concentration is

increased the absorbance will level off as is indeed the case for the results from both flame used. In the fuel lean flame the order of magnitude of interfering atom which increases the absorption is of the same order of its ionization potential $Rb > Cs > K > Na$.

Since Li compounds have the highest dissociation energies, competition for OH from other alkali metals with the possible exception of Cs would be insignificant. In the case of Cs, the Li - absorbance is slightly smaller than that of Rb, although Cs is almost completely ionized in the flame. In considering its hydroxide, CsOH is more stable than RbOH. This may be sufficient to tie up the Cs atom as CsOH and the free electron contribution from Cs will be less hence ground state Li atoms in this case will be less than when Rb is added as the Li will tend to ionize to a greater degree.

In the case of Na, the effect is quite straight forward. The enhancing effect of K, Rb and Cs are in the order of **decreasing** ionization potential and for the fuel lean flame the effect is less in magnitude

than the fuel rich one. The exceptional case is that of Li added, Na - absorbance is depressed, an explanation of this effect is follows: Comparing the D_0^0 of the NaOH to that of Li, it is very much smaller than that of Li compound. The equilibrium involving the Li compound will be in favor of the compound formation and causes the reduction in atomic Li. This in turn will cause the decrease in electron concentration and can be represented by following equilibrium



LiOH is very stable hence the above equilibrium will shift in favor of compound formation and Li atom concentration is reduced. The equilibrium



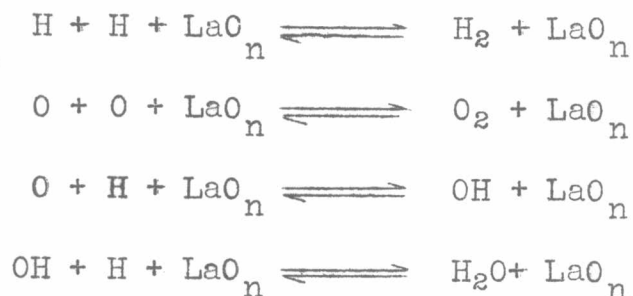
will readily shift RHS and cause the decrease in electron concentration in the system. Na is more easily ionized so that in order to maintain the steady state, the ionization equilibrium of Na will shift in the direction of ion production resulting in a decrease in Na - absorption. Between difference flames the effect

is also of different order. This can be considered in a way that in fuel rich flame $[H]$ is very much larger than in fuel lean flame. The equilibrium will shift to increase the Li atom concentration considerably more than the fuel lean flame. This makes the effect in ^{the} fuel lean flame less in magnitude than in the fuel rich flame.

In the case of K-absorbance, the enhancing effect due to the interfering atoms added is of the order $Cs > Rb > Na > Li$ and corresponds to the trend in ionization potential. Li shows the least effect because of its highest ionization potential which hardly causes an increase in electron concentration in the system. Another factor which make Li of the least effect is the higher stability of LiOH. When Na was added up to 100 ppm the effect is suddenly less than that of Li. This can be seen from Table III that in both flames Na and Li ions are present in nearly equal concentrations which implies that both contribute equal concentrations of electrons to the system. So in this case the stability of hydroxide has to be taken into consideration that is that

LiOH is very stable caused a decrease in $[OH]$ in the flame. Hence the K atom is present in larger amounts and causes the absorbance to increase somewhat. For Cs, although its hydroxide is most stable next to that of Li it has the lowest ionization potential so that the electron supply to the flame is much greater than that of other alkali metals. Once the $[e]$ in the flame is high the equilibrium in equation $e^- + M^+ \rightleftharpoons M^0$ will shift in favor of the atom production. Because K atoms in the ground state are present in greater numbers the absorbance is increased.

Consider the three species system of K-Cs with the addition of La. La is one of the lanthanide series which can form stable or refractory oxide compounds in the flame. These oxides act as a third body in the flame by these reactions

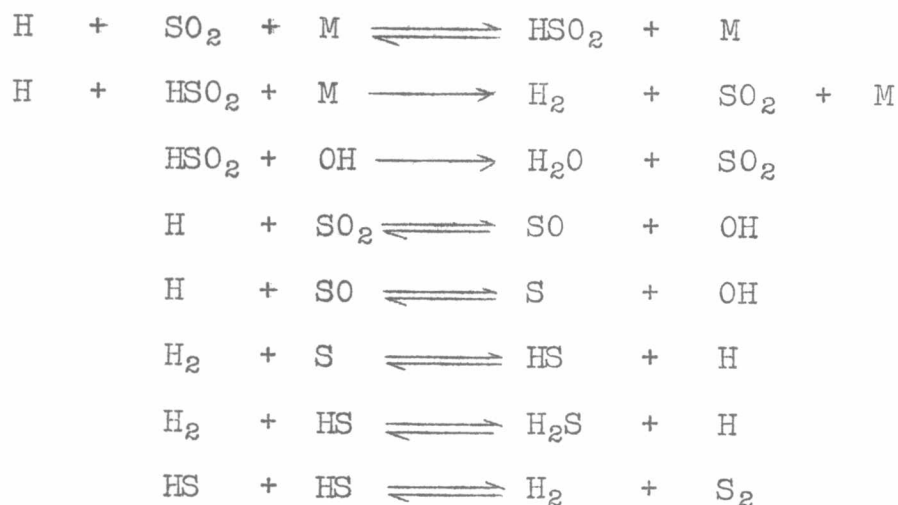


This will result in the decrease of active species in the flame hence the K-atom is even more released as a ground state atom. Although K atoms are increased by the addition of more easily ionizable Cs atom, the presence of lanthanum oxide increases even more than the absorbance of potassium. This agreed with the result that when concentration of La^{+3} is increased five-fold the absorbance is increased even more.

Another possible mechanism is that lanthanum oxide may act something like a radical scavenger. It takes up the active flame species to large extent and causes the reduction in concentration of radicals in the system. Again, the value of ionization potential of La also can be taken into consideration. It has a low value and therefore La will ionize contributing [e] to the system. By these means the K ionization equilibrium will shift in the direction of the ground state atom increasing the K-absorbance. This is a probable reason why the difference in magnitude is observed in both flames.

Discussion for anion effect

The effect of anions also was investigated but not in a great detail. From figure (8) it is seen that in the determination of Na at a very low concentration of 0-1 ppm the $\text{SO}_4^{=}$ and Cl^- salts do give the different in absorption. $\text{SO}_4^{=}$ gives a higher absorption. This is because of the effect of $\text{SO}_4^{=}$ in the flame. When $\text{SO}_4^{=}$ solution was introduced, it can dissociate into many species such as SO_2 , SO_3 , SO , S_2 , HS etc. It is found that $\text{SO}_4^{=}$ also reacts (19) with active species in the flame by these reactions.



From these reactions the concentration of active atomic flame species is reduced which subsequently diminishes

the formation of Na compounds. This results in the absorbance for the $\text{SO}_4^{=}$ salt being greater than that of the Cl^- salt.

The case of NO_3^- and Cl^- for K atom, the explanation of the phenomena is believed to be very much the same for that of $\text{SO}_4^{=}$. In general, any anion in the flame can cause the variation of absorbance to a lesser or greater extent.

Conclusion

From this study, it can be concluded that interelement interferences between alkali metals can influence the accuracy of an alkali metal analysis if care is not be taken in the determinations. In most cases there is a maximum interference, of a certain concentration of interfering atoms added where the absorbance attains a maximum. With higher concentration the effect will level off. In carrying out an analytical analysis, the concentration of interfering atoms should be above the amount where maximum absorbance is obtained. Not only will the sensitivity be improved, but also

an additional error in the absorbance value will be eliminated.

In this work, the discussion of the results is somewhat qualitative because of many problems encountered. One of the problems is that the concentration of active species in the flames could not be calculated. A shielded or separated flame was not available for this work and temperature measurements could not be done as the necessary equipment was not available. However temperature measurement in the flame can be done relatively easily by the method provided by Winefordner (20). Secondly the type of burner used produced an unshielded flame causing the unknown amount of oxygen to enter the flame system by diffusion making it impossible to obtain an accurate estimate of oxygen supplied to the flame. Improving of the flame can be done by using the shielded burner or using inert gas as a shielding film around the flame. By this process the oxygen intake in the system can be controlled and providing the temperature is known, concentrations of reactive species in flame can be calculated.

From this study, it is evident that an alkali metal has a significant effect on the behaviour of another alkali metal in the flame. Care must be taken when performing alkali metal analyses to determine what other alkali metals are also present. A certain minimum concentration of the interfering metal should be maintained.

The addition of La to the alkali metal also increases the absorbance quite considerably. Its mechanism is different from those of alkali metal in a way that La formed stable compound in the flame acting as a third body and also as a radical scavenger. Its use in alkali metal analyses bears further investigation.

There are other group of elements such as alkaline earths whose absorbances in flames are affected by the presence of other elements. Studies similar to the present work could be carried out on many other systems.

Appendix I

Calculation of the fuel-oxidant ratio

Flame I.

$$\text{C}_2\text{H}_2 \text{ flow rate} = 1.50 \quad \text{l/m}$$

$$\text{air flow rate} = 11.50 \quad \text{l/m}$$

$$\text{O}_2 \text{ in take} = 2.30 \quad \text{l/m}$$

Using

$$PV = nRT$$

$$P = 1 \text{ atm.}$$

$$V = 2.30 \quad \text{l/m}$$

$$R = 82.054 \times 10^{-3} \text{ l-atm deg}^{-1} \text{ mole}^{-1}$$

$$T = 300^\circ\text{K}$$

$$n_{\text{O}_2} = 0.0934 \quad \text{mole}$$

$$n_{\text{C}_2\text{H}_2} = 0.0609 \quad \text{mole}$$

$$\text{C}_2\text{H}_2 : \text{O}_2 = 1 : 1.53$$

Flame II

$$\text{C}_2\text{H}_2 \text{ flow rate} = 0.8 \quad \text{l/m}$$

$$\text{air flow rate} = 11.5 \quad \text{l/m}$$

$$n_{\text{O}_2} = 0.0934 \quad \text{mole}$$

$$n_{\text{C}_2\text{H}_2} = 0.0325 \quad \text{mole}$$

$$\text{C}_2\text{H}_2 : \text{O}_2 = 1 : 2.87$$

Appendix II

Calculation for the Standard Deviation

NaCl 1 ppm was used for each run

| no | Reading % T | | | | av. | x Abs. | d= \bar{x} -x | d ² |
|----|-----------------|-----------------|-----------------|-----------------|-------|------------------|---------------------|----------------|
| | 1 st | 2 nd | 3 rd | 4 th | | | | |
| 1 | 63.5 | 64.5 | 63.5 | 63.0 | 63.62 | 0.1965 | 0.0012 | 0.000014 |
| 2 | 62.5 | 62.5 | 62.5 | 62.0 | 62.37 | 0.2048 | -0.0071 | 0.000050 |
| 3 | 62.5 | 62.5 | 62.5 | 62.0 | 62.37 | 0.2048 | -0.0071 | 0.000050 |
| 4 | 62.5 | 62.5 | 62.5 | 63.0 | 62.62 | 0.2034 | -0.0057 | 0.000032 |
| 5 | 63.5 | 62.5 | 63.0 | 62.5 | 63.12 | 0.2000 | -0.0023 | 0.000005 |
| 6 | 63.0 | 63.0 | 63.0 | 63.5 | 63.12 | 0.2000 | -0.0023 | 0.000005 |
| 7 | 63.0 | 64.0 | 64.0 | 63.0 | 63.50 | 0.1972 | 0.0005 | 0.000002 |
| 8 | 65.0 | 64.5 | 64.0 | 65.5 | 64.75 | 0.1887 | 0.0090 | 0.000081 |
| 9 | 64.5 | 64.0 | 64.0 | 64.0 | 64.12 | 0.1931 | 0.0046 | 0.000021 |
| 10 | 64.5 | 65.0 | 64.0 | 64.5 | 64.25 | 0.1921 | 0.0056 | 0.000021 |
| 11 | 64.0 | 63.0 | 63.5 | 64.0 | 63.87 | 0.1945 | 0.0032 | 0.000021 |
| | | | | | | $\bar{x}=0.1977$ | $\sum d^2=0.000299$ | |

$$\begin{aligned}
 \text{Standard Deviation } \sigma &= \pm \sqrt{\frac{\sum d^2}{N}} \\
 &= \pm \sqrt{\frac{0.000299}{11}} \\
 &= \pm \sqrt{0.000027} \\
 &\approx \pm 0.005
 \end{aligned}$$