2. Chemical Interferences:

(I) Formation of Compounds of Low Volatility:

- The most common type of interference is *by anions* that form compounds of low volatility with the analyte and thus reduce the rate at which the analyte is atomized. The decrease in calcium absorbance that is observed with increasing concentrations of sulfate or phosphate.
- Example of *cation interference* have also been recognized. Aluminum is found to cause low results in the determination of magnesium, apparently as a result of the formation of a heat-stable aluminum/magnesium compound.

Solutions:

- *Higher temperature*
- *Releasing agents: cations that react preferentially with the interferants* and prevent its interaction with the analyte, e.g; addition of an excess of Sr or La minimizes the interference of phosphate in the determination of Ca
- *Protection agents: form stable but volatile species with the analytes (i.e. EDTA,APDC….). e.g;* 8-hydroxyquinoline suppresses the interference of aluminum in the determination of calcium and magnesium.

(II) Dissociation Equilibria:

Gaseous environment of a flame or a furnace, numerous dissociation and association reactions lead to conversion of the metallic constituents to the elemental state. Some of these reactions are reversible

$$MO \rightleftharpoons M + O$$

$$M(OH)_2 \rightleftharpoons M + 2OH$$

Where M is the analyte atom.

$$VO_x \rightleftharpoons V + O_x$$

$$AlO_x \rightleftharpoons Al + O_x$$

$$TiO_x \rightleftharpoons Ti + O_x$$

(III) Ionization Equilibria:

✓ Ionization of atoms and molecules is small in combustion mixtures that involve air as the oxidant, and generally can be neglected.

✓ In higher temperatures of flames where oxygen or nitrous oxide serves as the oxidant, however, ionization becomes important, and a significant concentration of free electrons exists

$$M \rightleftharpoons M^+ + e^- \qquad K = [M^+][e^-] / [M]$$

✓ if the medium contains not only species M but species B as well, and if B ionizes, then the degree of ionization of M will be decreased by the mass-action effect of the electrons formed from B.

$$B \rightleftharpoons B^+ + e^-$$

TABLE 9-2 Degree of Ionization of Metals at Flame Temperatures*

Element	Ionization Potential, eV	Fraction Ionized at the Indicated Pressure and Temperature			
		$p = 10^{-4}$ atm		$p = 10^{-6}$ atm	
		2000 K	3500 K	2000 K	3500 K
Cs	3.893	0.01	0.86	0.11	>0.99
Rb	4.176	0.004	0.74	0.04	>0.99
K	4.339	0.003	0.66	0.03	0.99
Na	5.138	0.0003	0.26	0.003	0.90
Li	5.390	0.0001	0.18	0.001	0.82
Ba	5.210	0.0006	0.41	0.006	0.95
Sr	5.692	0.0001	0.21	0.001	0.87
Ca	6.111	3×10^{-5}	0.11	0.0003	0.67
Mg	7.644	4×10^{-7}	0.01	4×10^{-6}	0.09

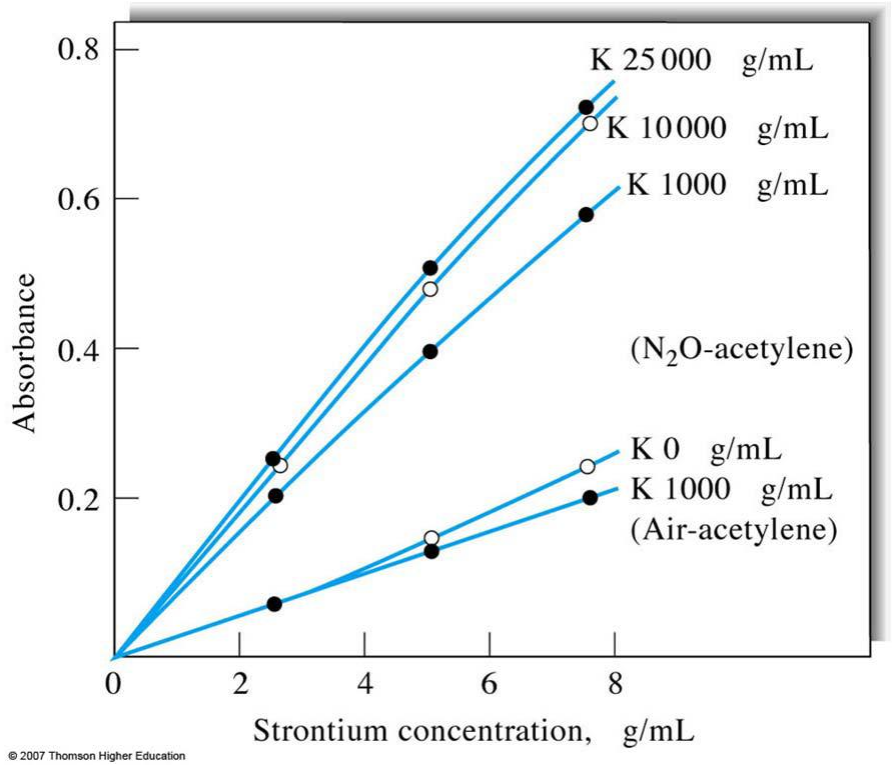
*Data from B. L. Vallee and R. E. Thiers, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 6, p. 3500. New York: Interscience, 1965. Reprinted with permission of John Wiley & Sons, Inc.

A decrease in concentration of atoms resulting from ionization occurs. Thus, under some circumstances decrease in emission or absorption may be observed in hotter flames.

Solution: *ionization suppressor* which provides a relatively high concentration of electrons to the flame; suppression of ionization of the analyte results.

B can then act as an *ionization suppressor.*

Effect of K concentration on calibration curve for Sr



- Note the significant increase in slope of these curves as strontium ionization is repressed by the increasing concentration of potassium ions and electrons.
- Note also the enhanced sensitivity produced by using nitrous oxide instead of air as the oxidant.
- The higher temperature achieved with nitrous oxide undoubtedly enhances the degree of decomposition and volatilization of the strontium compounds **in the flame.**