Chemiluminescence reactions involving hypohalites and related oxidants have been exploited for a wide variety of analytical applications, primarily for the determination of free chlorine, halides and a variety of compounds in pharmaceutical preparations and natural waters. Proposed mechanisms of the light-producing pathways are insufficiently supported by spectroscopic evidence but, where emission spectra are known, large differences show that numerous different emitters are involved. A deeper understanding of the light-producing pathways and hence the relationship between analyte structure and chemiluminescence intensity is required.

Two examples of the use of halates in chemiluminescence will now be mentioned. A novel flow-injection system for the determination of formaldehyde has been described. It is based on a strong enhancement by formaldehyde of the weak emission from the reaction between potassium bromate and rhodamine 6G in sulfuric acid. The method has been applied to determine formaldehyde in the air samples and a possible mechanism has been proposed.

The oxidation reaction between periodate and polyhydroxyl compounds has also been studied. A strong emission, especially in the presence of carbonate, is observed when the reaction takes place in a strongly alkaline solution (but not in acidic or neutral solution) without any other chemiluminescence reagent. Background and chemiluminescence signals of the sample are enhanced by oxygen and decreased by nitrogen. The chemiluminescence spectrum shows two main bands (at 436-446 nm and 471-478 nm). Based on these, a possible chemiluminescence mechanism has been proposed. Two emitters contribute to the chemiluminescence background, singlet oxygen and carbonate radicals.

The addition of polyhydroxyl compounds or hydrogen peroxide causes enhancement of the chemiluminescence signal. This reaction system has been developed as a flow injection assay for hydrogen peroxide, pyrogallol, and α-thioglycerol. The ions involved in the reaction - periodate, carbonate and hydroxyl - can be immobilized on a strongly basic anion-exchange resin and highly sensitive chemiluminescence flow sensors for each analyte have been assembled.