solvent chemistry for positive ions created wider, more diffused peaks, resulting in a reduction in the overall resolving power of the technique. The use of selective solvents therefore must be tempered to balance the need for identifying a complex mixture of analytes without jeopardizing instrument resolution. Though electrospray ionization is heavily dependent on concentration, which has been reported to provide better sensitivity for low volume samples [10], the addition of acid modifiers in the positive mode and methyl halides in the negative mode proved useful in allowing simultaneous ionization of analytes and increasing overall signal intensity of analytes. As a result, formic acid at a concentration of at least 2.5% (*v/v*) was found to show enhanced ionization efficiency in the positive ion mode when compared to solvents with less or no formic acid added (Figure 1).

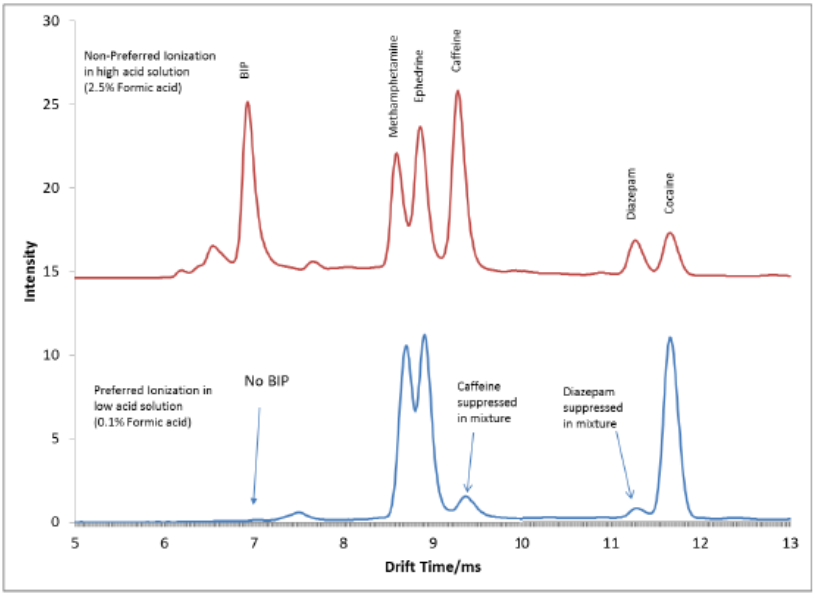

Figure 1. Analysis of 50ppm caffeine, (R)-methamphetamine, (S,R)-ephedrine, diazepam and cocaine using 2.5% formic acid (top) and 0.1% formic acid (bottom) of acid modifier using the RA4100.

In addition, changes in solvent chemistry were able to produce changes in the analyte ion species being formed in the negative mode.[11] Methyl halides specifically, chloroform at a concentration of 0.1% (*v/v*) was found to promote improved ionization efficiency in the negative ion mode. Other solvents such as ammonium nitrate proved useful in altering the ionic species being obtained for some analytes. For the positive ion mode, such solvent chemistries produced ammonium adducts $[M+NH_4]^+$ versus the typical protonated $[M+H]^+$ adducts. In the negative ion mode, this same solvent system produced $[M+NO_3]^-$ adducts versus the typical $[M-H]^-$ ions. However, it was also observed that the ionization of nitro-aromatics was suppressed in