B118 Ultraviolet (UV) Spectra of Synthetic Cathinones: Resurrecting an Old Technique

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After attending this presentation, attendees will understand the value of UV spectroscopy for distinguishing positional isomers of the synthetic cathinones. Attendees will also better understand how ortho, meta, and para alkyl substitution on the aromatic moiety in the synthetic cathinones produces predicable shifts in the major UV absorption bands. Observation of differences in the near UV spectra of positional isomers of synthetic cathinones can permit the differentiation of these isomers when the electron impact mass spectra of the isomers are uninformative, as is often the case.

This presentation will impact the forensic science community by demonstrating the utility of UV spectroscopy as a detection mode for liquid and supercritical fluid chromatography. A scheme for the prediction of the position of major UV absorption bands for synthetic cathinones having multiple substituted aromatic moieties will be presented.

UV spectroscopy was at one time a widely used instrumental method for the analysis of controlled substances. Analysts would record the near UV spectra of the suspected controlled substance in an appropriate solvent and then consult tables of λ_{max} values to make an identification; however, the latest Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) guidelines now relegate UV spectroscopy to Category C, the lowest category of analytical technique for the analysis of controlled substances. Nevertheless, for certain types of analytical problems confronting forensic drug chemists, UV spectroscopy may be very useful, if not indispensable. The synthetic cathinones are a case in point: their electron impact mass spectra (a Category A technique) typically show weak molecular ion peaks and uninformative fragmentation patterns. Their UV spectra often provide information about the substitution of the aromatic moiety in these compounds. The basic UV chromophore of the synthetic cathinones can be viewed as acetophenone. Acetophenone has four electronic transitions in the near UV: in n-hexane these bands are found at 238.7nm ($\varepsilon = 12,500$), 276.5nm ($\varepsilon = 900$), 285.2nm ($\varepsilon = 880$), and 321.0nm ($\varepsilon = 44$). The very weak 321.0nm transition is the $n \rightarrow \pi^*$ transition of the carbonyl; the remaining bands are $\pi \rightarrow \pi^*$ transitions involving the benzene ring. The strongest band is designated $^1B_{1u} \leftarrow {}^1A_{1g}$. The synthetic cathinones α-PVP, α-PBP, pentedrone, buphedrone, ethcathinone N,N'-dimethylmethcathinone, and methcathinone have an acetophenone-type structure with substitution on the acetophenone methyl group. When these compounds are analyzed by Ultra High-Performance Supercritical Fluid Chromatography (UHPSFC) with a near UV detector, spectra of these compounds were dominated by a strong peak at 238nm-239nm. Analysis of other synthetic cathinones under the same conditions demonstrated that ortho alkyl substitution increases the wavelength of the $^1B_{1u} \leftarrow {}^1A_{1g}$ transition by 0.9nm, meta alkyl substitution increases the wavelength of the band by 4.4nm, and para alkyl substitution increases the wavelength of the band by 10.9nm. For multiple substituted benzene rings, the effects of alkyl substitution are generally additive. Using the increment values for ortho, meta, and para alkyl substitution of 0.9nm, 4.4nm, and 10.9nm, respectively, yields the following predicted λ_{max} values for the $^1B_{1u} \leftarrow {}^1A_{1g}$ transitions of di-alkyl substituted cathinones: 2,3-dimethylmethcathinone 243.9nm (observed 243nm), 2,4-dimethylmethcathinone

250.4nm (observed 250nm), and 3,4-dimethylmethcathinone 253.9 nm (observed 254 nm). These results illustrate that near UV spectra can differentiate alkyl-substituted synthetic cathinones and that rules can be formulated for the prediction of the locations of UV transitions of new alkyl-substituted synthetic cathinones.

Cathinones, Ultraviolet Spectroscopy, Aromatic Substitution