A161 Anion Identification Via Complexation With Meso-Octamethylcalix(4)pyrrole and Electrospray Ionization Mass Spectrometry (ESI-MS) Detection

Sandra E. Rodriguez-Cruz, PhD, and Kathryn Carson, BS, Drug Enforcement Administration, Southwest Laboratory, 2815 Scott Street, Vista, CA 92081*

After attending this presentation, attendees will become familiar with a new method for the identification of counterions using the anion- binding agent meso-octamethylcalix(4)pyrrole and electrospray ionization mass spectrometry (ESI-MS) analysis.

This presentation will impact the forensic community by demonstrating a new technique to identify salt forms in forensic drug analysis.

Salt form identification has become routine in forensic drug analysis, as it could result in differences in sentencing based on salt form (i.e., cocaine HCl vs. cocaine base), and can also identify counterfeit pharmaceuticals. Currently acceptable anion identification techniques include precipitation tests, such as the $AgNO_3$ test, and infrared spectroscopy (IR). While precipitation tests can distinguish between halides, many other salt forms do not produce distinct results. IR spectra of different salt forms are not always distinguishable from one another, as is often observed in the analysis of black tar heroin. Nuclear magnetic resonance (NMR) results may also distinguish between the base form of a substance and a salt form, but specific identification of the anion is not possible.

The compound *meso*-octamethylcalix(4)pyrrole (C4P) is a member of a class of functionalized calix(4)pyrroles that have been the subject of recent research. It has been found that this class of molecules non- covalently coordinates to anions, producing a large ion with an overall negative charge. The soft ionization conditions of ESI-MS allow the complex to be transferred intact into the gas phase and subsequently into the MS detector, allowing collection of molecular weight data.

Subtracting the weight of the C4P (MW=428) gives the molecular weight of the anion.

A method for the identification of basic drug anions has been developed using a quadrupole ion-trap mass spectrometer with an ESI source. Solutions were prepared in acetonitrile at concentrations of 10-15 ug/ml and injected directly into the mass spectrometer via a syringe pump. Complex formation was achieved by the addition of 50 ul of a 0.5 mg/ml solution of C4P in acetonitrile to 1 ml of sample solution. Data was collected in both positive and negative ion modes for each sample; analysis of each sample was complete in two minutes or less.

Complexation with C4P was observed for chloride, bromide, iodide, acetate, and nitrate salts. Expected isotope ratios corresponding to chlorine and bromine were observed, providing further confirmation of formation of the anion-bound complex. Anion complexation was not observed for sulfate or phosphate salts. Anion selectivity tests were also performed by testing solutions with multiple anions in equimolar amounts. In accordance with other papers on the issue, chloride ions seemed to have a higher binding affinity to C4P than bromide ions.

It was determined that complexation of a sample with C4P and subsequent analysis by ESI-MS is a viable and rapid means for identification of many common anions found in forensic drug samples.

Electrospray Ionization, Forensic Drug Analysis, Anions

 ** Presenting Author*