A185 Infrared Identification of Heroin Salts

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The goal of this presentation is to examine the infrared identification of the salts of heroin, which can be problematic due to the formation of an amorphous state in the course of analysis. The precipitation behavior of heroin salts is fundamental to this discussion and the related issues of crystallization and hydration will be addressed. The discriminating features of infrared spectra will also be examined for the different halide salts of heroin.

This presentation will impact the forensic science community by describing an extraction procedure and recrystallization scheme that can facilitate the infrared identification of the salt forms of heroin in drug evidence.

Infrared spectroscopy has become an invaluable technique that is routinely used in the analysis of controlled substances. The technique can be readily applied to solid-dosage forms, which generally allows the chemical form of the substance (base, salt form, and hydration state) to be determined as part of the drug identity. The infrared spectrum of the solid-dosage form is a function of the crystalline structure of the substance. The molecular arrangement is highly symmetric in the crystal and presents a reproducible infrared spectrum that is usually characterized by a multitude of finely-detailed, sharp spectral features unique to the substance in a specific chemical form.

A limitation to the infrared analysis of solid-dosage forms is in the formation of an amorphous (non-crystalline) state for the drug substance that lacks the symmetry of periodic molecular packing. The spectra of amorphous solids are characterized by broad spectral features that lose much of the fine detail found in the spectrum of the crystalline state, which can make an infrared identification unreliable. Most controlled substances readily condense into a crystalline state and their infrared identification is routine; however, the salt forms of some opiates, and especially heroin, often precipitate as amorphous solids, which complicate their infrared analysis.

The formation of heroin salts is strongly influenced by the phenomenon of hydration, whereby water molecules participate in the molecular packing in the solid state. The common solid-dosage form of heroin is the hydrochloride salt, which forms a crystalline monohydrate phase and presents a distinctive infrared spectrum.[1] Hydration usually occurs during precipitation of a molecular crystal when water is present in the solvent, and thereby available to be integrated into the crystal structure as it assembles. Many drug substances that form a hydrated molecular crystal can also occur as an anhydrous phase (without any water), which consists of a different crystalline structure that is distinguishable by infrared spectroscopy.[2] Heroin hydrochloride can also condense into an anhydrous solid (its precipitation requires exceptionally dry solvents), although the infrared spectrum lacks significant fine detail that suggests an amorphous material.

A critical factor with the precipitation of the hydrochloride monohydrate crystal is the presence of sufficient water in the solvent system to accommodate the composition of the solid. Another issue is the rate of precipitation, where rapid condensation produces an amorphous hydrate with a spectrum unsuitable for identification. Impurities can also be a complicating factor, and especially O^6-monoacetylmorphine, a common breakdown product of heroin that arises from de-acetylation in the presence of moisture.

Recrystallization schemes that minimize impurities and favor the precipitation of the crystalline monohydrate phase will be presented. Heroin evidence often occurs as mixtures with other substances and can be relatively simple or complex (e.g., black tar heroin). One recrystallization procedure has proved generally successful for heroin evidence, although low purity samples of tar heroin (heroin less than 30%) remain problematic.

References:

[1]Balchin E, Malcolme-Lawes DJ, Rowe MD, Smith JAS, Bearpark MJ, Steed JW, Wu W, Horsewill AJ, Stephenson D. The unusual solid state structure of heroin hydrochloride monohydrate and its selective detection using NQR spectroscopy. New Journal of Chemistry, 2004; 28: 1309-1314.

1. Chappell J, Lee M. Hydration polymorphism of 3,4-methylenedioxymethamphetamine hydrochloride. Microgram, 1999; 32: 159-167.

Heroin Hydrochloride, Infrared Spectroscopy, Molecular Crystallization

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