B21 Comparison of Extraction in a Drop and Solid Phase Microextraction

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Upon completion of this presentation, participants should have a better understanding of two newer extraction methods.

This research involves the comparison and evaluation of two analytical separation techniques, solid phase microextraction (SPME) and extraction in a drop (ED). These two techniques have been evaluated for the extraction of commonly encountered drug materials of forensic interest.

The solid phase microextraction technique was developed a number of years ago [1] and has begun to have significant applications in many fields[2] including some application to forensic science problems. The extraction in a drop technique first appeared in the literature more recently[3] and few forensic applications have been reported in the literature[4,5].

In the solid phase microextraction (SPME) technique the actual extractant is a thin film of a non-volatile liquid coated on silica fibers, similar to the interior of a capillary gas chromatographic column. A bundle of these fibers are dipped into an aqueous solution containing the target compounds, which then partition between the supported liquid phase and the aqueous phase. In the extraction in a drop (ED) the process is analogous to the classic liquid/liquid extraction. However, by using a single microliter size drop hanging on the end of a micro syringe submerged in the aqueous solution, the extraction in a drop technique miniaturizes liquid/liquid extraction by a factor of many thousands.

For both the ED and the SPME experiments five milliliters of the solution to be extracted was placed in a small conical vial. For the ED experiments a five-microliter syringe with a Chaney adapter was used to draw up one microliter of the extraction solution and then inserted into the solution so the tip was several millimeters below the surface of the liquid. The extraction solution was then gently expelled from the tip to form a hanging drop. For the SPME experiments the fiber holder was placed into the vial with the fiber withdrawn into the protective barrel. The fiber was then extended so that it was also several millimeters below the surface of the solution. In both cases the solution was stirred with a triangular Teflon coated stirrer bar designed to fit the conical bottom of the vial. The solution was stirred at a moderate rate, so as not to knock the hanging drop off the end of the syringe. In all the ED experiments pristane was used as internal standard in the extraction solvent. When the extraction period was over, the drop was drawn back into the syringe or SPME fiber into the protective holder and then withdrawn from the vial and immediately placed into the injector port of the GC/MS at 250ºC.

Initial experiments were done with cocaine hydrochloride solutions at fifty or one hundred micrograms per milliliter. The solutions were made in a pH 5.5 citrate buffer because some preliminary work indicated reproducibility problems in the absence of the buffer. It was found that that both ED and SPME extracted cocaine well from such solutions. It was found that at the above concentrations the SPME method required only one to two minutes to obtain strong signals in the GC/MS and with ED thirty seconds to a minute were adequate.

The methods were compared using a cough and cold Elixir containing phenyl propanolamine (12.5 mg/5ml), Brompheniramine maleate (2 mg/5ml) and Dextromethorphan (10 mg/5ml). It was diluted with an equal volume of buffer solution (Citrate 5.5) and then extracted as above. The ED extractions provided readily detectable peaks in ten seconds and sizable peaks for all three drug components in sixty seconds. In fact, the longer times were problematic because glycerol caused chromatographic problems that obscured the phenyl propanolamine peak. Again with SPME, identifiable peaks were seen after short extraction times and the peak sizes reach a maximum at a five to ten minute extraction time.

The effect of concentration on extraction efficiency also were studied with a four drug mixture made up in a pH 10 buffer solution. This drug mixture contained pseudoephedrine at 120mg/100ml, doxylamine at 25mg/100ml, dextromethorphan at 40mg/100ml and acetaminophen at 1000mg/100ml. The selection of the pH 10 buffer was dictated by the insolubility of the acetaminophen at lower pH values. Four additional serial dilutions were made producing five concentrations ranging from base to one-sixteenth of the base concentration. These were examined for extraction times from thirty seconds to two minutes. Although acetaminophen was the largest component, it extracted and chromatographed poorly. It was detectible in the majority of extractions, but gave a broad peak with poor reproducibility.

Using ED at the base concentration good-sized peaks were obtained even at short extraction times. At one to eight and one to sixteen dilutions the pseudoephedrine was not seen and extraction times of about a minute were required for good peaks from the doxylamine & dextromethorphan. Using the SPME, with the same solutions, it was found that pseudoephedrine did not extract. The other two components gave good results when extracted from the base solution and one to two dilution in thirty seconds and with the higher dilutions in a minute or less.

Conclusions:

- Both ED and SPME are very rapid and useful methods of performing microextractions of a variety of drug substances.
- ED does not require any equipment that is not immediately available in most crime laboratories. SPME does

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require purchase of a holder and some coated extraction fibers for an initial cost of several hundred dollars.

- At the concentration ranges of interest for street drug analysis, the extractions will usually require a minute or less for either technique.
- Using ED one can try a variety of different solvents very quickly to find the most suitable. SPME actually offers a wider range of extraction conditions since a number of different fibers are commercially available.
- Both techniques are better for qualitative analysis than quantitative analysis although with proper controls quantitative analysis can be performed. With ED the use of an internal standard in the extraction solvent simplifies quantitative analysis.
- SPME is the more mature technique with hundreds of paper having been published including some applications to forensic problems.
- ED is much newer and has been less researched, but appears to offer some real potential for a number of forensic applications.

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Sample Preparation, Drug Analysis, Extraction

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