Use of Sorbent Coated Metal Probes with Direct Analysis in Real Time (DART) Ionization for Rapid Analysis of Herbal Supplements

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Abstract

Determination of composition and quality of herbal supplements are time consuming due to the nature of the active components and complexity of the sample matrix. Published methods often incorporate solid phase microextraction (SPME) of supplement extracts followed by either GC/MS or LC/MS analysis. More recently, flexible and rugged sorbent coated wire solid phase extraction devices have been produced for use in simplifying sample prep. We utilized these wires for both sample extraction and as a support for direct surface desorption ionization facilitating rapid analysis. Comparison of the results using this new direct analysis from sortbent coated wire method with analysis of liquid samples from syringe-based and column-based solid phase extraction devices using bare wire screens will be shown.

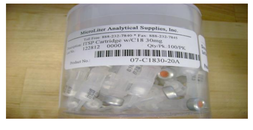
Experimental

Extracts of herbal supplements were prepared using published protocols. The extracts were analyzed by using three methods.. The solutions were vortexed for 30 seconds and centrifuged for 5 minutes at 3000 RPM. 1 mL of the solution was removed and put in its own vial to be used with the various SPE techniques. The original analysis showed spectra dominated by carbohydrates. Solid phase extraction techniques were then used to improve signal to noise ratios .

Extraction Techniques

ITSP Solutions SPE cartridges

- Cartridges were conditioned with methanol and then a water wash.
- The sample (100 µL) was ejected through the cartridge.
- Water was then used again as a wash.
- Methanol was used as the elutent and the aliquot was collected and analyzed via DART.



The Evol-XR syringe micro extraction by packed sorbent (MEPS) syringes made by SGE

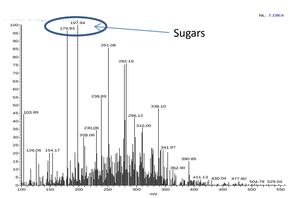
- The syringe needle is coated with a C18 sorbent material that facilitates the extraction.
- The syringe needle was conditioned with the same procedure as the ITSP-SPE.
- The aliquot of the methanol elutent was analyzed with the DART.

SPME LC Probes made by Supelco

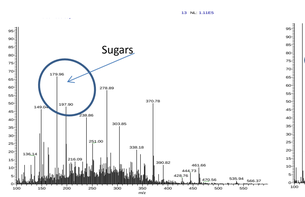
- Rugged fibers are coated in a C18 sorbent material.
- Preconditioned in 15% H_2O in methanol and then 15% methanol in H_2O. T
- hey were then exposed directly to the extracts and analyzed with the DART.

DART MS of Supplement Extracts

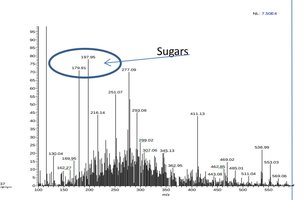
Spectra Heavily Influenced by Presence of Sugar



Above is the spectra for a commercial Black Cohosh supplement



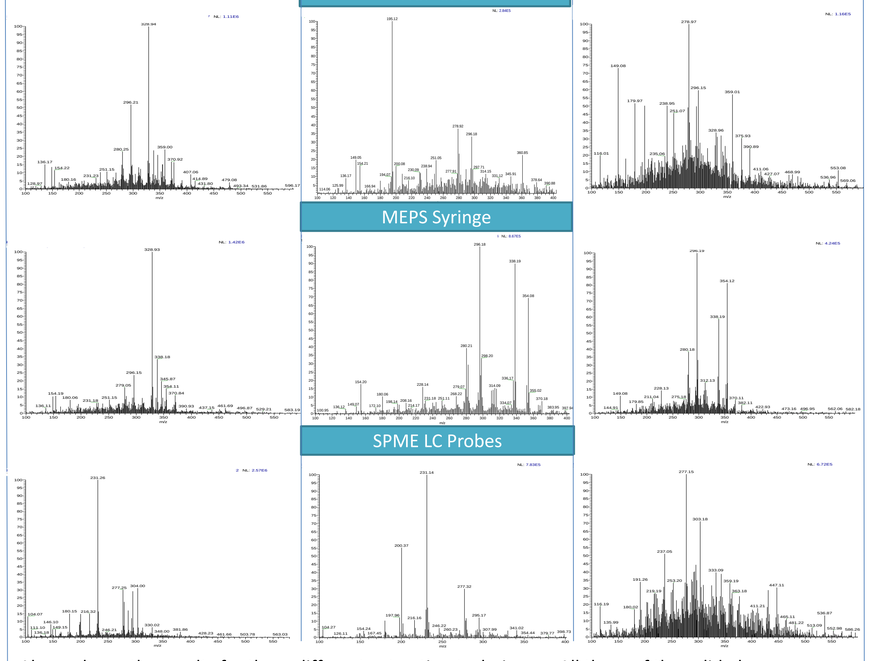
Above is the spectra for finely ground Black Cohosh root



Above is the spectra for a commercial St. John Wort supplement

SPE Techniques for Sugar Removal

Black Cohosh Herb	Black Cohosh Supplement	St. Johns Wort Supplement
	ITSP-SPE	
	MEPS Syringe	
	SPME LC Probes	

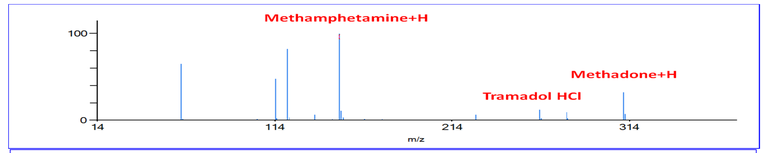


Above shows the results for three different extraction techniques. All three of the solid phase extractions techniques successfully removed the sugars from the extract which was to be expected. The SPME LC probes provided the fastest and simplest extraction. The MEPS syringe provided the most information rich spectra.

The time it takes to use each technique was also something considered in this study. The ITSP-SPE Cartridges and MEPS syringe were both the same at about 30-45 minutes. The SPME were slightly longer at an hour. Sample spotting should also be taken into consideration with these techniques. The SPME LC probes can be analyzed directly with DART making them very fast once the extraction time is complete. The ITS-SPE cartridges and the MEPS syringe required the sample to be spotted and allowed to dry which add some time to the process.

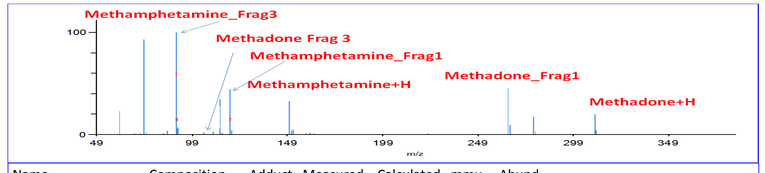
SPME of Narcotics in Urine

Solid phase micro-extraction(SPME) LC probes, part # 57281-U, a 45µm C18-silica coated metal alloy 22 gauge wire, were used for rapid isolation and then DART analysis of drugs present in urine. The SPME LC probes were condition in DI H_2O with 10% methanol and then with methanol with 10% H_2O. The SPME coated portion of the probe is then submerged in the urine sample for 30 minutes. Finally, the probes are dipped into water to remove salts and non-bound material. The probe is then passed through the heated gas exiting the DART source. The MS spectra were collected using JEOL AccuTOF in under 10 seconds per analysis. The reusable probes were cleaned by submerging the probe in acetonitrile post-analysis.



Name	Composition	Adduct	Measured	Calculated	mmu	Abund.
Tramadol HCl	C16H25NO2		263.18671	263.18854	1.83	12.215
± Methadone	C21H27NO	+H	310.21561	310.21708	1.48	32.321
Methamphetamine	C10H15N	+H	150.12849	150.12828	-0.22	100.000

Human urine has matrix effects that can make identifying compounds of interest difficult. Use of the SPME LC probes helped extract and concentrate the ions of interest rapidly. Total sampling time from start to finish is ≈ 45 minutes.



Name	Composition	Adduct	Measured	Calculated	mmu	Abund.
± Methadone	C21H27NO	+H	310.21719	310.21708	-0.11	19.796
± Methadone_Frag1	C19H21O		265.15979	265.15924	-0.55	45.780
± Methadone_Frag3	C7H5O		105.03360	105.03404	0.44	2.354
Methamphetamine	C10H15N	+H	150.12720	150.12828	1.08	36.947
Methamphetamine_Frag1	C9H11		119.08350	119.08607	2.57	45.745
Methamphetamine_Frag2	C7H7		91.05400	91.05477	0.77	100.000

The anticipated fragmentation pattern was obtained on a high resolution JEOL DART AccuTOF MS and was used as confirmation.

Conclusion

- All three extraction techniques removed the sugars from the supplements.
- SPME LC probes were the easiest to use and were sampled directly.
- MEPS syringe provided the most information rich data.
- The SPME LC probes successfully isolated drugs from urine and permit direct desorption ionization.

Acknowledgements

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