

NCFS Sample Preparation and Instrumental Parameters

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Prepared by Dana-Marie Dennis and Jessica Frisch

Addenda by Dana-Marie Dennis and Quashanna Price

1. MICROMETRY

- A stage micrometer is used to calibrate the Leica Stereomicroscope micron bar in order to make measurements of the smokeless powder kernels. Measurements are made in millimeters rounded to one decimal place.
- The smokeless powder kernels are placed on a white background, and a total of fifty kernels are photographed. The micrographs are taken at x10.1 magnification.
- Double-sided tape is used to stand kernels, such as short tubed powders upright, so that micrographs may be taken to facilitate length measurements. Length measurements are not recorded for discs and flattened ball samples.
- ImageTool software is used to calibrate the micron bar and make measurements of each of the kernels in the micrographs. Calibration of the micron bar is done when the micrograph image is at a zoom of 1:1 and measurements are taken when the micrograph image is at a zoom of 1:2. The software is available from <http://compdent.uthscsa.edu/dig/itdesc.html>
- The averages and standard deviations of the measurements are calculated and the maximum and minimum measurements are noted for the 50 kernels measured.

2. GC-MS

2.1. Extraction

- The smokeless powders are cut, and approximately 10 mg of the cut kernels are placed into a previously weighed small vial. Preliminary work indicates that cutting the kernels is necessary for the optimal extraction of the analytes.
- 300 μL of methylene chloride with 10 ppm undecane are added to the contents of the tube to facilitate extraction of the target analytes (undecane functions as an internal standard). The tube is allowed to sit for three hours.
- Remove the supernatant from the vial and place into GC vial (with 200 μL vial insert) for analysis. A 1:10 dilution is also analyzed.

2.2. Analysis

- Analyses of the samples are conducted using a Hewlett-Packard 6890 gas chromatograph interfaced to a 5973 mass spectrometer. **Addendum (as of July 2013): Analyses of the samples are conducted using an Agilent 7890A gas chromatograph interfaced to a 5975C inert XL EI/CI MSD with Triple-Axis detector. The instrument is operated in electron ionization mode.**
- The 30m capillary column is an HP-5MS 5% phenyl methyl siloxane with a nominal diameter of 250.00 μm and a film thickness of 0.25 μm . **Addendum (as of July 2013): Restek Rtx-5MS 30m x 250.00 μm x 0.25 μm .**
- Helium carrier gas is maintained at a flow rate of 1.2 mL/min on the column with an average velocity of 40 cm/sec.
- One microliter injections of the sample are introduced using an Agilent ALS autosampler G2614A splitless injector. **Addendum (as of July 2013): One microliter injections of the sample are introduced using an Agilent ALS autosampler G4513A splitless injector.**
- The mass spectrometer transfer line is maintained at 250°C, with a source temperature of 230°C.
- Mass spectra are scanned between 43 and 400 m/z . The solvent delay is 4.00 minutes.
- The injection port temperature was maintained at 170°C.
- The initial oven temperature of 40°C is held for 1 minute, followed by a temperature ramp of 25°C/min to a final temperature of 280°C, which is held for three minutes.
- Positive identification of an analyte is determined by a 3:1 signal-to-noise ratio in the TIC or EIC, the presence of at least three major ions, and its retention time compared to the standard.

3. ATR-FTIR

3.1. Extraction

- Approximately 2.5 mg of uncut smokeless powder kernels are added to a small vial with 80 μL of acetone and allowed to sit for thirty minutes.
- The supernatant is spotted on a microscope slide, the solvent allowed to evaporate, followed by another application of the supernatant (added as a second layer to the first spot) and subsequent solvent evaporation. The film is analyzed using ATR-FTIR.

3.2. Analysis

- Analyses of the samples are conducted on an ATI Mattson Infinity Series FTIR and Spectra Tech IR Plan Advantage IR microscope. **Addendum (as of September 2014): Analyses of the samples are conducted using a Bruker LUMOS (© Bruker Optik GmbH2012)**
- The internal reflectance element used to analyze the sample is silicon. **Addendum (as of September 2014): The internal reflectance element is germanium.**
- Four spectra from four different areas of the film are collected in absorbance mode using OMNIC software with the number of scans totaling 32 and a resolution of 4 cm^{-1} . The data is collected within the $4000 - 400\text{ cm}^{-1}$ range. An ATR correction was plied using the OMNIC software which corrects for the variance in the penetration depth. The data image is reported in percent transmittance. The spectrum with the flattest baseline and best resolution is chosen and presented in transmittance. **Addendum (as of September 2014): Four spectra from four different areas of the film are collected in absorbance mode using OPUS software (version 7.2 Build: 7, 2, 139, 1294) with the number of scans totaling 64 and a resolution of 4 cm^{-1} . The data is collected within the $4000 - 600\text{ cm}^{-1}$ range. The spectrum with the flattest baseline and best resolution is chosen and presented in transmittance.**

Analyte	CAS Number	<i>m/z</i>	% Abundance*
Nitroglycerin	55-63-0	46	100
		76	15
		43	13
Camphor	21368-68-3	95	100
		81	64
		108	41
Dibutyl Phthalate	84-74-2	149	100
		223	6
		205	5
Diethyl Phthalate	84-66-2	149	100
		177	26
		105	7
Dipentyl (Amyl) Phthalate	131-18-0	149	100
		150	9
		237	8
Diphenylamine	122-39-4	169	100
		84	10
		51	7
Dioctyl Phtalate	117-81-7	149	100
		167	35
		57	17
Ethyl Centralite	85-98-3	120	100
		148	81
		268	46
Methyl Centralite	611-92-7	134	100
		240	62
		106	45

Analyte	CAS Number	<i>m/z</i>	% Abundance*
2,4-Dinitrotoluene	121-14-2	165	100
		89	50
		63	27
4-Nitrodiphenylamine	836-30-6	214	100
		167	83
		184	26
2-Nitrodiphenylamine	119-75-5	214	100
		167	82
		180	37
4-Nitrosodiphenylamine	156-10-5	167	100
		198	72
		184	12
Undecane**	1120-21-4	57	100
		43	72
		71	55

Table 1: List of analytes, CAS Numbers, and Three Major Ions (*m/z*) with Relative Intensities of the Target Analyte

- * % Abundance determined using standards and in-house GC-MS method
- ** denotes internal standard