Method Validation and Detection of Adulterants in 1582 Seized Drug Exhibits by High Resolution Mass Spectrometry
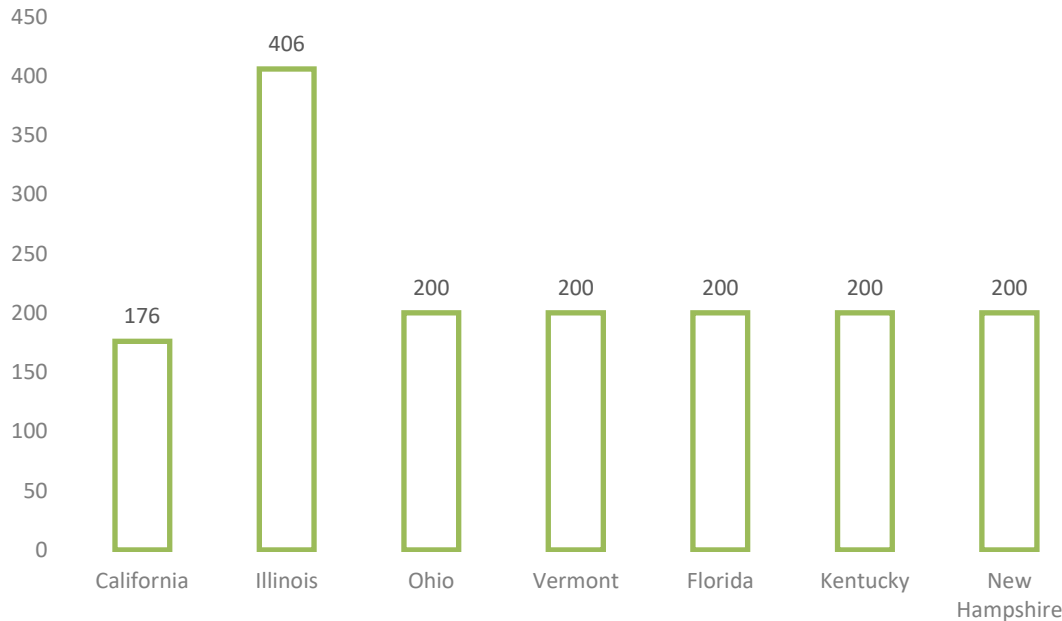
Taís R. Fiorentin, PhD; Amanda Mohr, MS, D-ABFT-FT, Melissa F. Fogarty, MS, D-ABFT-FT; David M. Martin, PhD, Thom Browne, MS; Trisha L. Conti, PhD; Allison Standifer, MS; Linda Bouchard, BS; Michael Gilbert, BS; Timothy Tripp, BS; Jennifer Watson, BS; Susan Molloy, BS; Barry K. Logan, PhD, F-ABFT.*

Background

- Cutting agents
  - Diluents (pharmacologically inactive)
  - Adulterants (pharmacologically active)
- Changes over time increasing the risks to the user's health
  - 1980's – present: lidocaine, caffeine, phenacetin, diltiazem, hydroxyzine, levamisole, benzocaine, acetaminophen, procaine, aminopyrine, prilocaine, bicarbonate, starch and sugars
- Underreport of substances

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Samples

Number of Samples

State	Number
California	176
Illinois	406
Ohio	200
Vermont	200
Florida	200
Kentucky	200
New Hampshire	200

➢ 1582 drug evidence received from June 2020 to November 2020
  ➢ 27 samples: no results
  ➢ 1555 samples included

➢ Samples shipped deidentified

➢ In-house identifying number
  • Date of receipt by the originating lab
  • County of origin

Methods

- Thermo Scientific™ Vanquish™ UHPLC system coupled with a Thermo Scientific™ Q Exactive™ Plus Hybrid Quadrupole-Orbitrap™ mass spectrometer (LC-QE-MS)

- Data processed using TraceFinder Clinical software
  - Version 4.1

- Column:
  - Thermo Scientific™ Accucore™ Vanquish™ C18+ UHPLC column (100 x 2.1 mm, 2.6 μm)

- Mobile Phase:
  - A: 0.1% formic acid in water
  - B: 0.1% formic acid in acetonitrile

- Dried samples reconstituted in 1000 μL MP

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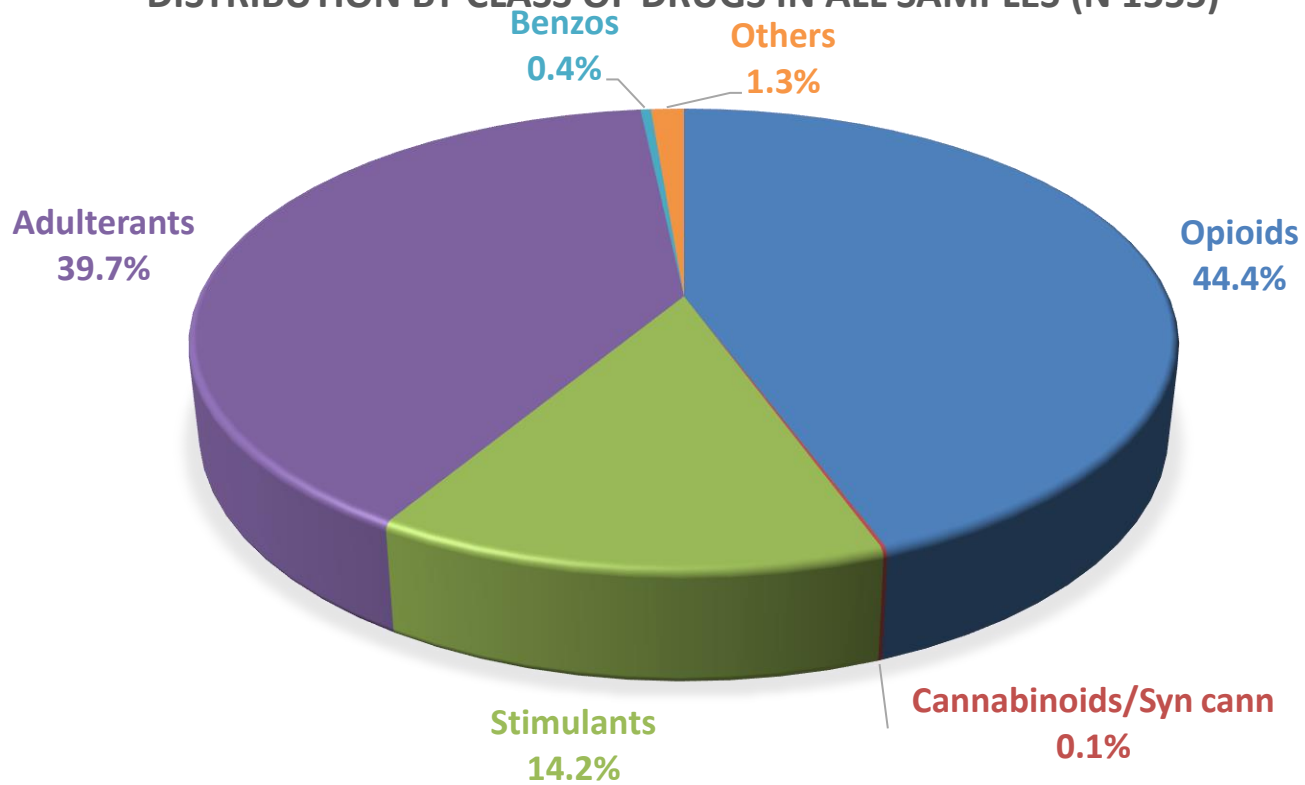# Methods

Method Validation

- 52 substances

- The developed method was validated in accordance with the UNODC and SWGDRUG guidelines

- Testing included:
  - Precision
  - Limit of Detection
  - Carryover

Results

DISTRIBUTION BY CLASS OF DRUGS IN ALL SAMPLES (N 1555)

- Benzos 0.4%
- Others 1.3%
- Adulterants 39.7%
- Opioids 44.4%
- Cannabinoids/Syn cann 0.1%
- Stimulants 14.2%

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Results

Distribution by class of drugs in each state
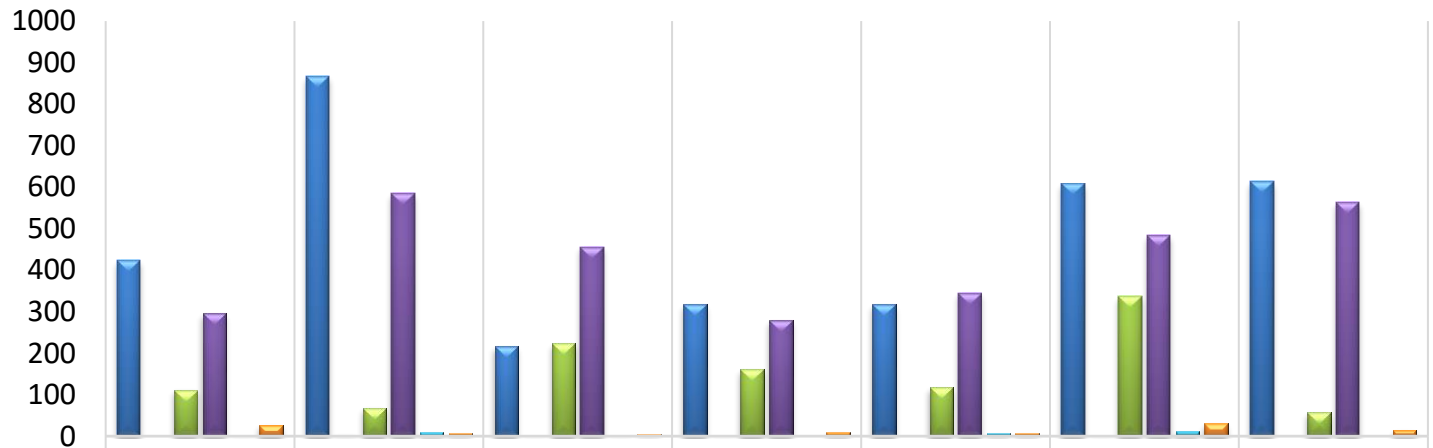
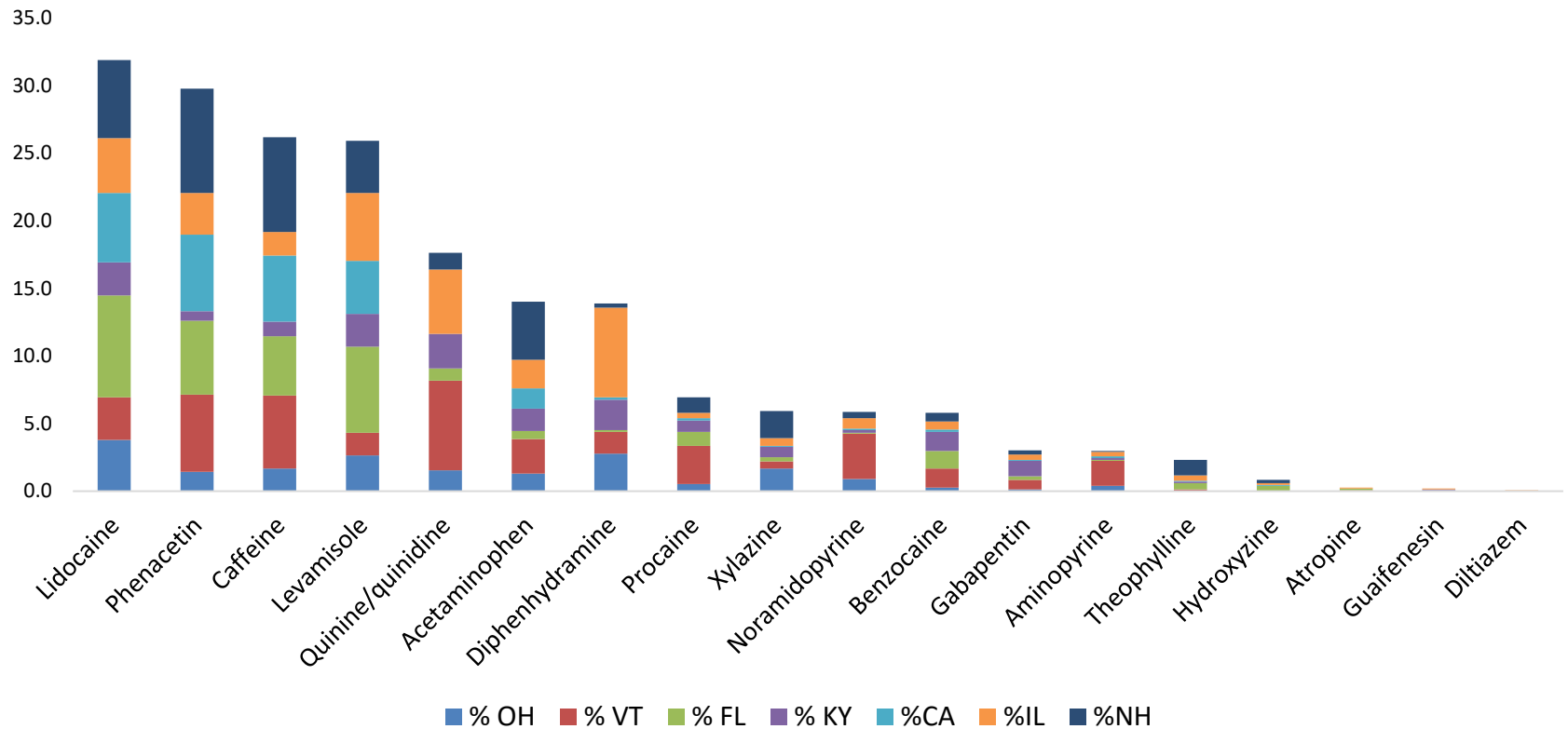|	OH	VT	FL	KY	CA	IL	NH
Opioids	423	867	217	318	318	608	614
Cannabinoids/Syn cann	0	3	2	2	0	2	0
Stimulants	111	68	223	161	118	336	57
Adulterants	296	585	456	278	345	484	564
Benzos	2	9	2	1	6	11	0
Others	27	6	5	9	6	30	15

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Results

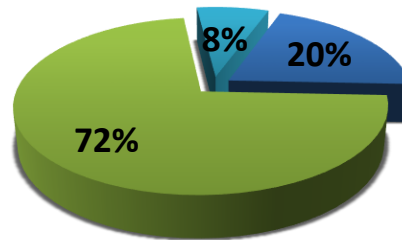Number of Toxic Adulterants found in each State
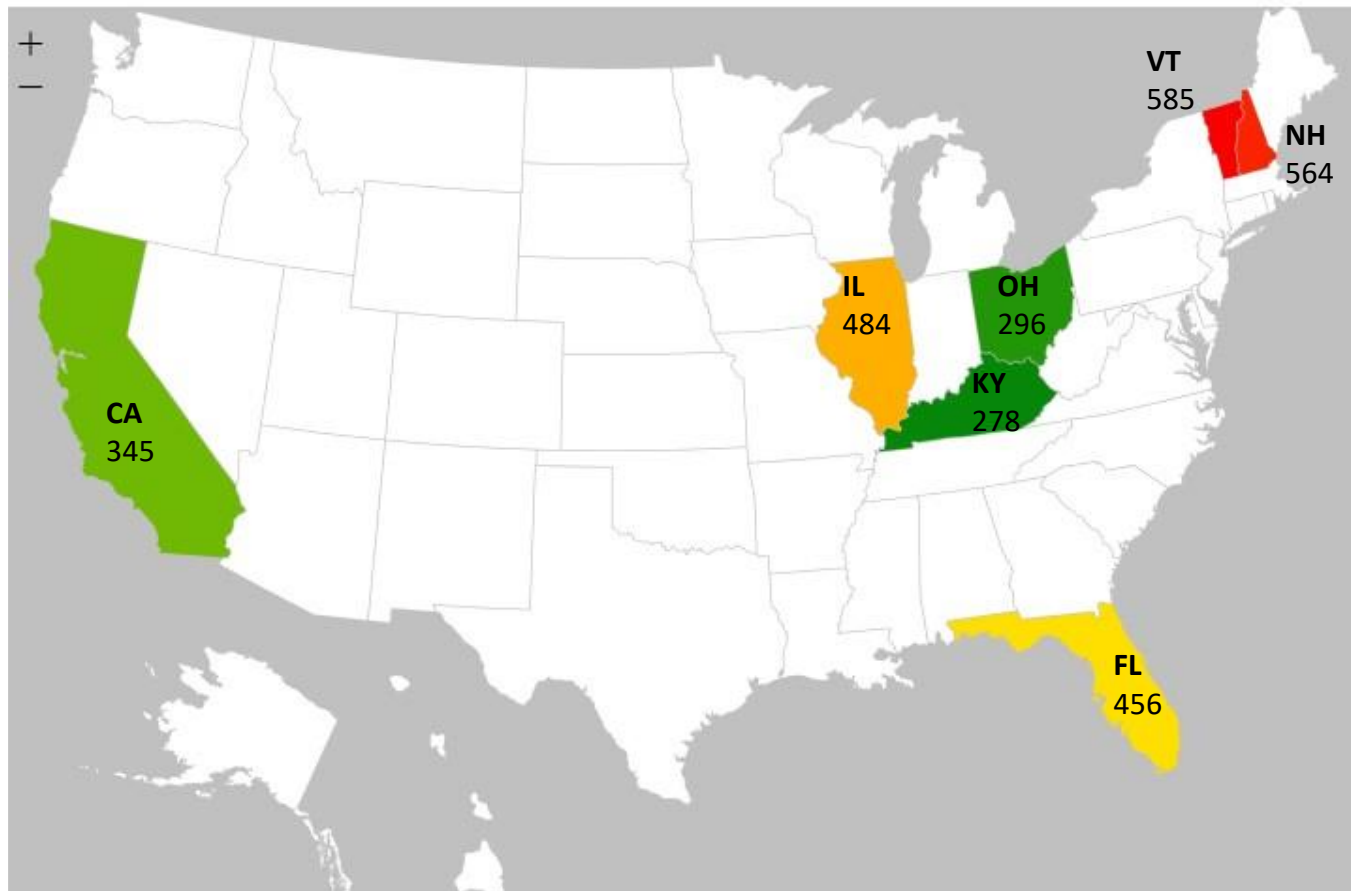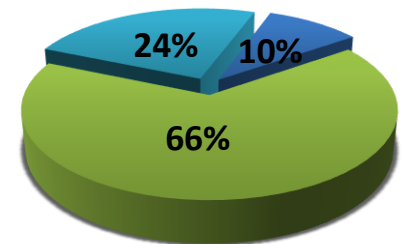
Results

Percentage of Adulterants in each state

Results

Legend:
- No Toxic Adulterants
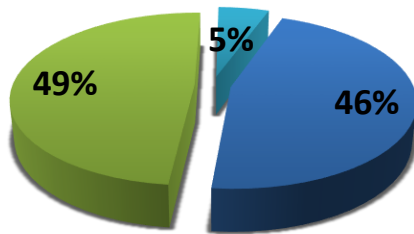- 1-4 Toxic Adulterants
- 5-8 Toxic Adulterants
- 9+ Toxic Adulterants

California (n=174)
- 8%
- 20%
- 72%

Vermont (n=194)
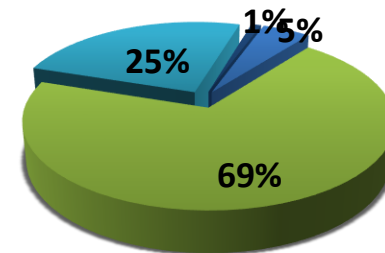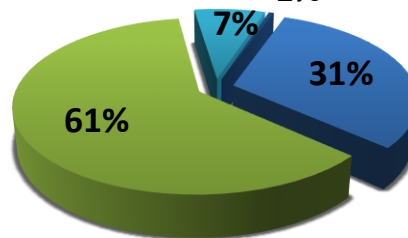- 24%
- 10%
- 66%

Illinois (n=399)
- 5%
- 46%
- 49%

Ohio (n=190)
- 1%
- 7%
- 31%
- 61%

New Hampshire (n=200)
- 1%
- 5%
- 25%
- 69%

Florida (n=200)
- 10%
- 16%
- 74%

Kentucky (n=198)
- 11%
- 50%
- 39%

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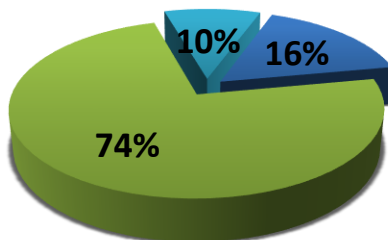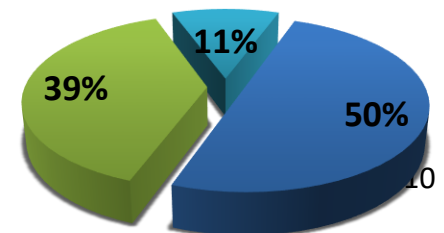
Toxic Effects

- Caffeine – stimulant
  - Minority effects: headache, irritability, mood disturbances, anxiety and sleep disturbance
- Quinine/Quinidine – antimalarial/antiarrhythmics
  - Cardiovascular toxicity: abnormal heart rhythms and hemolysis. Mimics the "rush" on heroin use by the hypotensive effect and similar bitter taste
- Lidocaine– local anesthetic
  - Associated with cardiovascular problems: myocardial depression, hypotension, bradycardia and arrhythmias
  - 2018 FDA warning: risk of methemoglobinemia
- Phenacetin – analgesic/antipyretic
  - Can cause nephrotoxicity and hepatotoxicity, suspected carcinogenicity
- Levamisole – antihelminthic
  - Neutropenia, agranulocytosis, arthralgias, methaemoglobinaemia, purpura retiform and skin necrosis
  - Deaths reported as a result of complications secondary to levamisole-tainted cocaine

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Discussion

- Tramadol trending in opioid samples
- Heroin and Opium samples in Iran (Akhgari et. al, 2018)

JOURNAL OF PSYCHOACTIVE DRUGS 455

Table 1. The most prevalent active pharmaceutical ingredients in illicit psychoactive drugs detected using HPLC and GC/MS instrumentation in Tehran, Iran.

Seized psychoactive drug	Combined hidden active pharmaceutical ingredients (number)
Methamphetamine	Methamphetamine+ Phenmetrazine+ Pseudoephedrine+ Dextromethorphan (3)
	Methamphetamine+ Caffeine+ Phenmethrazine+ Pseudoephedrine (2)
	Methamphetamine+ Caffeine+ Ecstasy (1)
	Methamphetamine+ Phenmethrazine (1)
	Methamphetamine+ Ketamine (1)
	Methamphetamine (2)
Iranian crack (Heroin)	Heroin+ Morphine+ Codeine+ Papaverine+ Noscapine+ Phenobarbital+ Acetaminophen+ Tramadol+ Caffeine(2)
	Heroin+ Morphine+ Codeine+ Papaverine+ Noscapine+ Methamphetamine+ Chloroquine+ Methadone (2)
	Heroin+ Morphine+ Codeine+ Papaverine+ Noscapine+ Chloroquine+ Methadone+ Caffeine (1)
	Heroin+ Morphine+ Codeine+ Caffeine (3)
	Heroin+ 6-Monoacetylmorphine+ Caffeine (2)
Ecstasy	3,4- Methylenedioxymethamphetamine+ Methamphetamine (4)
	3,4- Methylenedioxymethamphetamine (4)
	3,4- Methylenedioxymethamphetamine+ Heroin (2)
Opium	Morphine+ Codeine+ Papaverine+ Noscapine+ Acetaminophen (6)
	Morphine+ Codeine+ Papaverine+ Noscapine+ Acetaminophen+ Chloroquine (2)
	Morphine+ Codeine+ Papaverine+ Noscapine+ Chloroquine+ Tramadol (2)

Akhgari et. Al 2018. The Texture of Psychoactive Illicit Drugs in Iran: Adulteration with Lead and other Active Pharmaceutical Ingredients. Journal of Psychoactive Drugs,v. 50, n. 5, 451–459.

Class	Substances		n
	Fentanyl		645
	Heroin		431
		6-MAM	448
		Acetylcodeine	393
		Morphine	358
		Codeine	263
		Ethylmorphine	8
Opioids	Acetylfentanyl		397
	Tramadol		284
	Butyryl Fentanyl		83
	Oxycodone		35
	Thebaine		13
	Furanylfentanyl		4
	U-47700		3

Heroin by-product

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Acknowledgements

- CFSRE
- The Colombo Plan
- Vermont Forensic Laboratory
- Kentucky State Police Central Forensic Laboratory
- New Hampshire State Police Forensic Laboratory
- Pinellas County Forensic Lab
- Illinois State Police
- Miami Valley Regional Crime Laboratory
- OPD Criminalistics Division

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Questions?

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