

Pesticide Residue Analysis Using Pressurized Liquid Extraction (PLE) for the Analysis of Pesticides in Foods by GC/MS.

Introduction

In recent years, increased awareness of consumer and food safety has led to a greater demand for screening of various food stuffs. This includes screening for multi residue pesticides. Like most agricultural products, pesticides are widely used for crop management and can find their way into consumer goods. It is therefore important that reliable, rapid and cost effective procedures be in place for the screening of products destined for a consumer market.

Pesticide extractions and analysis have long been in place for the food and environmental industries. Tapping into these methodologies, the usage of Pressurized Liquid Extraction can be fitted to deliver a one step extraction and extract clean-up process for rapid GC/MS analysis of a wide array of pesticides.

Instrumentation

- FMS, Inc. PLE® extraction system
- Thermo TSQ Quantum Ultra

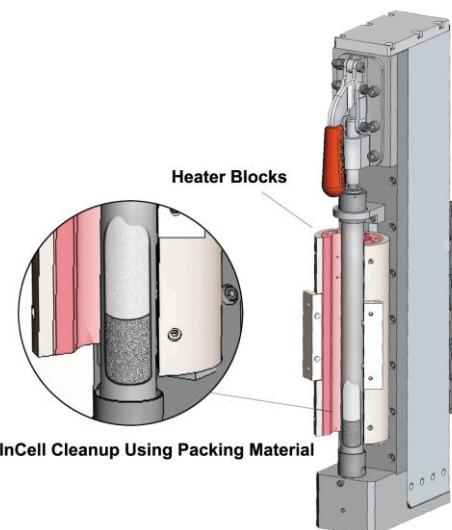
Consumables

- FMS 10 mL PLE extraction cells
- FMS Teflon PLE end caps
- Acetonitrile, pesticide grade
- FMS CleanXtract™ Cleanup
- Ottawa Sand
- Nine individual pesticide mixes standards for total of 203 pesticides.
- Internal standard.

Sample/Reagent Prep

1. Sample aliquots are to be weighed out, thoroughly homogenized.
2. Extraction cells are filled from bottom to top.
3. Cover bottom frit with sufficient Ottawa Sand.
4. Add sample aliquot on top of Sand.
5. Add relevant standard mixes and internal standards.

Figure #1. PLE extraction cell with sample and in-line clean-up.



Sample/Reagent Prep

5. Add FMS CleanXtract™ mix in the cell on top of Sample
6. Add Ottawa Sand if needed to top off cell and place the cell in FMS extraction system.

PLE Procedure

Pesticides

1. Cells are filled with Acetonitrile.
2. Cells are pressurized for 5 min. Cells are cooled and depressurized
3. Cells are flushed with Acetonitrile and nitrogen purged of remaining solvent.
4. Final extract is collected and a sample aliquot is transferred to a vial for GC/MS analysis.

GC/MS Analysis

GC/MS-MS Conditions

Thermo Trace GC w/PTV

TSQ Quantum Ultra

30 meter, .25mm, .25µm Column w/5 meter Guard column

203 Pesticides scanned (414 transitions)

Results Table 1.

Analyte	LCS		Green Tea		Black Tea		Fennel Seed		Astragalus Root		Harthorn		Gota Kola Berry		Green Coffee	
	amt	rec	amt	rec	amt	rec	amt	rec	amt	rec	amt	rec	amt	rec	amt	rec
Organochlorine Pesticides																
Chlorneb	0.085	85%	0.095	95%	0.094	94%	0.072	72%	0.084	84%	0.091	91%	0.098	98%	0.084	84%
Pentachlorobenzene	0.061	61%	0.066	66%	0.066	66%	0.056	56%	0.049	49%	0.058	58%	0.061	61%	0.054	54%
HCH-alpha	0.085	85%	0.083	83%	0.079	79%	0.072	72%	0.075	75%	0.076	76%	0.088	88%	0.085	85%
Pentachloroanisole	0.071	71%	0.075	75%	0.08	80%	0.069	69%	0.064	64%	0.072	72%	0.078	78%	0.071	71%
HCH-beta	0.076	76%	0.08	80%	0.076	76%	0.064	64%	0.067	67%	0.078	78%	0.092	92%	0.079	79%
HCH-gamma (Lindane)	0.075	75%	0.081	81%	0.083	83%	0.067	67%	0.069	69%	0.078	78%	0.077	77%	0.089	89%
HCH-delta	0.082	82%	0.078	78%	0.07	70%	0.069	69%	0.069	69%	0.073	73%	0.072	72%	0.081	81%
Heptachlor	0.072	72%	0.083	83%	0.084	84%	0.073	73%	0.065	65%	0.075	75%	0.078	78%	0.078	78%
Pentachlorothioanisole	0.071	71%	0.075	75%	0.08	80%	0.069	69%	0.064	64%	0.072	72%	0.078	78%	0.071	71%
Aldrin	0.065	65%	0.062	62%	0.07	70%	0.054	54%	0.064	64%	0.063	63%	0.08	80%	0.078	78%
4,4'-Dichlorobenzophenone	0.074	74%	0.075	75%	0.079	79%	0.075	75%	0.063	63%	0.076	76%	0.078	78%	0.079	79%
Fenson	0.066	66%	0.071	71%	0.066	66%	0.073	73%	0.065	65%	0.069	69%	0.063	63%	0.067	67%
Isodrin	0.106	106%	0.079	79%	0.11	110%	0.115	115%	0.058	58%	0.12	120%	0.082	82%	0.089	89%
Heptachlor epoxide (isomer B)	0.053	53%	0.082	82%	0.099	99%	0.054	54%	0.069	69%	0.097	97%	0.091	91%	0.048	48%
Chlorbenside	0.07	70%	0.07	70%	0.064	64%	0.066	66%	0.052	52%	0.069	69%	0.063	63%	0.07	70%
trans-Chlordane	0.045	45%	0.054	54%	0.05	50%	0.041	41%	0.038	38%	0.049	49%	0.049	49%	0.048	48%
2,4'-DDE	0.072	72%	0.078	78%	0.082	82%	0.088	88%	0.073	73%	0.087	87%	0.083	83%	0.078	78%
Endosulfan I	0.08	80%	0.097	97%	0.097	97%	0.115	115%	0.078	78%	0.132	132%	0.111	111%	0.097	97%
cis-Chlordane	0.076	76%	0.077	77%	0.081	81%	0.101	101%	0.077	77%	0.096	96%	0.081	81%	0.072	72%
trans-Nonachlor	0.093	93%	0.085	85%	0.088	88%	0.097	97%	0.071	71%	0.103	103%	0.081	81%	0.082	82%
Chlorfenson (Ovex)	0.063	63%	0.073	73%	0.077	77%	0.1	100%	0.065	65%	0.078	78%	0.072	72%	0.074	74%
Dieldrin	0.088	88%	0.127	127%	0.1	100%	0.103	103%	0.091	91%	0.089	89%	0.138	138%	0.097	97%
4,4'-DDE	0.062	62%	0.078	78%	0.085	85%	0.088	88%	0.068	68%	0.084	84%	0.068	68%	0.075	75%
2,4'DDD	0.086	86%	0.079	79%	0.089	89%	0.058	58%	0.074	74%	0.069	69%	0.113	113%	0.079	79%
Endrin	0.073	73%	0.085	85%	0.085	85%	0.177	177%	0.095	95%	0.086	86%	0.204	204%	0.159	159%
Ethylan (Perthane)	0.076	76%	0.073	73%	0.075	75%	0.095	95%	0.072	72%	0.084	84%	0.078	78%	0.078	78%
Endosulfan II	0.082	82%	0.083	83%	0.086	86%	0.052	52%	0.07	70%	0.071	71%	0.097	97%	0.078	78%
4,4'-DDD	0.086	86%	0.081	81%	0.093	93%	0.049	49%	0.072	72%	0.069	69%	0.103	103%	0.075	75%
2,4'-DDT	0.085	85%	0.083	83%	0.085	85%	0.072	72%	0.075	75%	0.063	63%	0.11	110%	0.078	78%
cis-Nonachlor	0.071	71%	0.064	64%	0.076	76%	0.044	44%	0.062	62%	0.054	54%	0.096	96%	0.062	62%
4,4'-Methoxychlor olefin	0.087	87%	0.102	102%	0.097	97%	0.062	62%	0.084	84%	0.073	73%	0.11	110%	0.079	79%
4,4'-DDT	0.086	86%	0.091	91%	0.094	94%	0.058	58%	0.085	85%	0.078	78%	0.12	120%	0.086	86%
2,4'-Methoxchlor	0.096	96%	0.097	97%	0.096	96%	0.07	70%	0.095	95%	0.087	87%	0.132	132%	0.111	111%
Mirex	0.081	81%	0.079	79%	0.087	87%	0.079	79%	0.066	66%	0.06	60%	0.102	102%	0.073	73%
Organonitrogen Pesticides																
2,6-Dichlorobenzonitrile	0.073	73%	0.077	77%	0.081	81%	0.067	67%	0.068	68%	0.068	8%	0.077	77%	0.073	73%
Biphenyl	0.068	68%	0.072	72%	0.079	79%	0.06	60%	0.065	65%	0.062	62%	0.08	80%	0.075	75%
3,4-Dichloroaniline	0.066	66%	0.073	73%	0.073	73%	0.064	64%	0.067	67%	0.067	67%	0.07	70%	0.067	67%
Tetrachloronitrobenzene (Tecnazene)	0.072	72%	0.059	59%	0.064	64%	0.051	51%	0.055	55%	0.059	59%	0.064	64%	0.049	49%
THPI (Tetrahydrophthalimide)	0.117	117%	0.128	128%	0.106	106%	0.102	102%	0.106	106%	0.1	100%	0.125	125%	0.121	121%
Diphenylamine	0.072	72%	0.078	78%	0.075	75%	0.071	71%	0.076	76%	0.073	73%	0.091	91%	0.078	78%
2,3,5,6-Tetrachloroaniline	0.084	84%	0.091	91%	0.086	86%	0.083	83%	0.085	85%	0.09	90%	0.101	101%	0.088	88%
Pebulate	0.074	74%	0.075	75%	0.083	83%	0.079	79%	0.074	74%	0.071	71%	0.079	79%	0.07	70%
N-(2,4-Dimethylphenyl)formamide	0.089	89%	0.089	89%	0.087	87%	0.09	90%	0.078	78%	0.084	84%	0.088	88%	0.088	88%
Propachlor	0.096	96%	0.107	107%	0.132	132%	0.1	100%	0.108	108%	0.103	103%	0.115	115%	0.106	106%
Cycloate	0.079	79%	0.087	87%	0.093	93%	0.077	77%	0.083	83%	0.083	83%	0.094	94%	0.08	80%
cis-Diallate	0.062	62%	0.081	81%	0.081	81%	0.064	64%	0.068	68%	0.067	67%	0.095	95%	0.073	73%
trans-Diallate	0.069	69%	0.072	72%	0.081	81%	0.074	74%	0.073	73%	0.056	56%	0.071	71%	0.063	63%
Propyzamide	0.081	81%	0.092	92%	0.099	99%	0.083	83%	0.08	80%	0.071	71%	0.09	90%	0.079	79%
Triallate	0.078	78%	0.083	83%	0.091	91%	0.074	74%	0.074	74%	0.081	81%	0.087	87%	0.077	77%
Dimethachlor	0.09	90%	0.097	97%	0.097	97%	0.089	89%	0.086	86%	0.11	110%	0.106	106%	0.101	101%
Propanil	0.069	69%	0.099	99%	0.071	71%	0.067	67%	0.069	69%	0.067	67%	0.067	67%	0.108	108%
Acetochlor	0.074	74%	0.088	%	0.085	85%	0.086	86%	0.074	74%	0.088	88%	0.103	103%	0.063	63%
Alachlor	0.088	88%	0.076	76%	0.089	89%	0.082	82%	0.08	80%	0.078	78%	0.095	95%	0.077	77%
Propisochlor	0.092	92%	0.122	122%	0.096	96%	0.08	80%	0.093	93%	0.103	103%	0.125	125%	0.097	97%
Linuron	0.082	82%	0.103	103%	0.101	101%	0.104	104%	0.079	79%	0.102	102%	0.124	124%	0.113	113%
Metolachlor	0.09	90%	0.1	100%	0.099	99%	0.134	134%	0.112	112%	0.1	100%	0.106	106%	0.112	112%
Diphenamid	0.071	71%	0.082	82%	0.082	82%	0.097	97%	0.071	71%	0.084	84%	0.094	94%	0.085	85%
Flutolanil	0.089	89%	0.089	89%	0.085	85%	0.228	228%	0.111	111%	0.156	156%	0.1	100%	0.109	109%
Pretilachlor	0.067	67%	0.077	77%	0.066	66%	0.126	126%	0.085	85%	0.101	101%	0.068	68%	0.024	24%
Oxadiazon	0.067	67%	0.064	64%	0.061	61%	0.1	100%	0.065	65%	0.074	74%	0.07	70%	0.071	71%
Norflurazon	0.096	96%	0.101	101%	0.079	79%	0.085	85%	0.088	88%	0.09	90%	0.12	120%	0.082	82%
Methoxychlor	0.096	96%	0.097	97%	0.096	96%	0.07	70%	0.095	95%	0.087	87%	0.132	132%	0.111	111%
Fenpropatrin	0.072	72%	0.093	93%	0.077	77%	0.052	52%	0.074	74%	0.059	59%	0.124	124%	0.099	99%
Pyridaben	0.073	73%	0.048	48%	0.08	80%	0.055	55%	0.06	60%	0.063	63%	0.062	62%	0.104	104%
Fluquinconazole	0.082	82%	0.085	85%	0.089	89%	0.055	55%	0.076	76%	0.065	65%	0.095	95%	0.082	82%
Etridiazole	0.088	88%	0.082	82%	0.089	89%	0.075	75%	0.088	88%	0.086	86%	0.105	105%	0.085	85%
Attrazine	0.103	103%	0.093	93%	0.095	95%	0.095	95%	0.066	66%	0.094	94%	0.082	82%	0.084	84%
Terbutylazine	0.073	73%	0.102	102%	0.072	72%	0.093	93%	0.092	92%	0.11	110%	0.072	72%	0.085	85%

Results Table 1 (continued).

Analyte	LCS		Green Tea		Black Tea		Fennel Seed		Astragalus Root		Harthorn		Gota Kola Berry		Green Coffee	
	amt	rec	amt	rec	amt	rec	amt	rec	amt	rec	amt	rec	amt	rec	amt	rec
Organonitrogen Pesticides																
MGK-264 I	0.064	64%	0.064	64%	0.063	63%	0.073	73%	0.057	57%	0.053	53%	0.065	65%	0.067	67%
MGK-264 II	0.059	59%	0.057	57%	0.047	47%	0.068	68%	0.039	39%	0.059	59%	0.031	31%	0.055	55%
MGK-264*	0.0615	62%	0.0605	61%	0.055	55%	0.0705	71%	0.048	48%	0.056	56%	0.048	48%	0.061	61%
Penconazole	0.12	120%	0.131	131%	0.148	148%	0.192	192%	0.137	137%	0.18	180%	0.121	121%	0.134	134%
Triadimenol	0.075	75%	0.085	85%	0.075	75%	0.12	120%	0.076	76%	0.166	166%	0.144	144%	0.086	86%
Fipronil	0.055	55%	0.086	86%	0.089	89%	0.085	85%	0.07	70%	0.104	104%	0.076	76%	0.081	81%
Procymidone	0.054	54%	0.071	71%	0.067	67%	0.073	73%	0.076	76%	0.071	71%	0.091	91%	0.068	68%
Lenacil	0.098	98%	0.108	108%	0.118	118%	0.107	107%	0.109	109%	0.099	99%	0.132	132%	0.099	99%
Tebuconazole	0.051	51%	0.092	92%	0.084	84%	0.073	73%	0.079	79%	0.119	119%	0.103	103%	0.082	82%
Hexazinone (Velpar)	0.083	83%	0.092	92%	0.093	93%	0.076	76%	0.08	80%	0.078	78%	0.093	93%	0.052	52%
Iprodione	0.107	107%	0.083	83%	0.092	92%	0.083	83%	0.098	98%	0.092	92%	0.119	119%	0.064	64%
Pyriproxyfen	0.082	82%	0.083	83%	0.102	102%	0.068	68%	0.08	80%	0.078	78%	0.104	104%	0.078	78%
Synthetic Pyrethroid Pesticides																
Tefluthrin	0.074	74%	0.074	74%	0.081	81%	0.073	73%	0.075	75%	0.071	71%	0.079	79%	0.08	80%
Transfluthrin	0.091	91%	0.093	93%	0.1	100%	0.065	65%	0.07	70%	0.082	82%	0.095	95%	0.08	80%
Anthraquinone	0.001	1%	0.002	2%	0.001	1%	0.003	3%	0.002	2%	0.001	1%	0	0%	0	0%
Bioallethrin	0.1	100%	0.123	123%	0.088	88%	0.151	151%	0.103	103%	0.144	144%	0.084	84%	0.085	85%
Resmethrin (trans)	0.101	101%	0.091	91%	0.105	105%	0.066	66%	0.074	74%	0.072	72%	0.096	96%	0.085	85%
Tetramethrin I	0.062	62%	0.075	75%	0.064	64%	0.05	50%	0.046	46%	0.056	56%	0.158	158%	0.054	54%
Tetramethrin II	0.045	45%	0.059	59%	0.046	46%	0.059	59%	0.053	53%	0.061	61%	0.048	48%	0.041	41%
Tetramethrin*	0.0535	54%	0.067	67%	0.055	55%	0.0545	55%	0.0495	50%	0.0585	59%	0.103	103%	0.0475	48%
Bifenthrin	0.084	84%	0.08	80%	0.084	84%	0.058	58%	0.082	82%	0.071	71%	0.109	109%	0.092	92%
cis-Phenothrin	0.067	67%	0.09	90%	0.078	78%	0.05	50%	0.078	78%	0.073	73%	0.095	95%	0.076	76%
trans-Phenothrin	0.071	71%	0.083	83%	0.142	142%	0.079	79%	0.082	82%	0.074	74%	0.101	101%	0.09	90%
lambda-Cyhalothrin	0.084	84%	0.079	79%	0.082	82%	0.055	55%	0.081	81%	0.067	67%	0.105	105%	0.078	78%
Acinathrin	0.07	70%	0.071	71%	0.073	73%	0.057	57%	0.071	71%	0.071	71%	0.078	78%	0.068	68%
cis-Permethrin	0.085	85%	0.081	81%	0.087	87%	0.059	59%	0.077	77%	0.067	67%	0.104	104%	0.082	82%
trans-Permethrin	0.095	95%	0.093	93%	0.089	89%	0.061	61%	0.081	81%	0.085	85%	0.127	127%	0.094	94%
Cyfluthrin*	0.086	86%	0.082	82%	0.085	85%	0.051	51%	0.071	71%	0.073	73%	0.108	108%	0.085	85%
Cypermethrin*	0.070	70%	0.076	76%	0.085	85%	0.063	63%	0.076	76%	0.068	68%	0.115	115%	0.089	89%
Flucythrinate I	0.079	79%	0.081	81%	0.089	89%	0.049	49%	0.073	73%	0.0748	75%	0.11	110%	0.084	84%
Flucythrinate II	0.097	97%	0.094	94%	0.088	88%	0.061	61%	0.093	93%	0.084	84%	0.137	137%	0.106	106%
Fenvaleate R	0.083	83%	0.084	84%	0.081	81%	0.061	61%	0.08	80%	0.067	67%	0.096	96%	0.072	72%
Fenvaleate S	0.086	86%	0.088	88%	0.091	91%	0.055	55%	0.085	85%	0.063	63%	0.119	119%	0.075	75%
Methylated Herbicides																
2-Phenylphenol	0.08	80%	0.086	86%	0.101	101%	0.083	83%	0.087	87%	0.084	84%	0.093	93%	0.088	88%
Chlorpropham	0.084	84%	0.122	122%	0.1	100%	0.111	111%	0.094	94%	0.118	118%	0.111	111%	0.109	109%
Metalaxyl	0.06	60%	0.044	44%	0.078	78%	0.069	69%	0.095	95%	0.077	77%	0.076	76%	0.087	87%
DCPA methyl ester (Chlorthal-dimethyl)	0.072	72%	0.075	75%	0.092	92%	0.079	79%	0.07	70%	0.078	78%	0.079	79%	0.081	81%
Chlozolinate	0.126	126%	0.109	109%	0.124	124%	0.105	105%	0.092	92%	0.095	95%	0.095	95%	0.129	129%
Fluifop-p-butyl	0.057	57%	0.063	63%	0.07	70%	0.126	126%	0.073	73%	0.098	98%	0.072	72%	0.094	94%
Bromopropylate	0.084	84%	0.082	82%	0.085	85%	0.109	109%	0.09	90%	0.103	103%	0.094	94%	0.1	100%
Organophosphorus Pesticides																
Methacrifos	0.068	68%	0.085	85%	0.091	91%	0.076	76%	0.081	81%	0.081	81%	0.086	86%	0.086	86%
Sulfotep	0.075	75%	0.069	69%	0.083	83%	0.071	71%	0.076	76%	0.078	78%	0.087	87%	0.088	88%
Terbufos	0.065	65%	0.068	68%	0.075	75%	0.075	75%	0.081	81%	0.083	83%	0.106	106%	0.091	91%
Tolclofos-methyl	0.076	76%	0.082	82%	0.085	85%	0.086	86%	0.076	76%	0.073	73%	0.086	86%	0.082	82%
Fenchlorphos (Ronnel)	0.075	75%	0.081	81%	0.085	85%	0.076	76%	0.076	76%	0.087	87%	0.082	82%	0.094	94%
Malathion	0.08	80%	0.098	98%	0.084	84%	0.107	107%	0.106	106%	0.112	112%	0.119	119%	0.111	111%
Fenthion	0.072	72%	0.093	93%	0.097	97%	0.109	109%	0.093	93%	0.094	94%	0.087	87%	0.087	87%
Bromophos methyl	0.076	76%	0.08	80%	0.093	93%	0.099	99%	0.093	93%	0.094	94%	0.07	70%	0.085	85%
Chlorfenvinphos (trans)	0.06	60%	0.106	106%	0.083	83%	0.129	129%	0.107	107%	0.123	123%	0.093	93%	0.081	81%
Bromophos ethyl	0.06	60%	0.07	70%	0.077	77%	0.112	112%	0.082	82%	0.106	106%	0.08	80%	0.077	77%
Iodofenphos	0.08	80%	0.082	82%	0.06	60%	0.126	126%	0.066	66%	0.1	100%	0.071	71%	0.08	80%
Ethion	0.09	90%	0.092	92%	0.081	81%	0.072	72%	0.076	76%	0.086	86%	0.127	127%	0.093	93%
Chlorthiophos I	0.057	57%	0.088	88%	0.066	66%	0.1	100%	0.061	61%	0.085	85%	0.085	85%	0.118	118%
Chlorthiophos II	0.07	70%	0.059	59%	0.041	41%	0.111	111%	0.063	63%	0.069	69%	0.077	77%	0.07	70%
Chlorthiophos III	0.062	62%	0.077	77%	0.08	80%	0.122	122%	0.076	76%	0.101	101%	0.061	61%	0.073	73%
Chlorthiophos*	0.063	63%	0.075	75%	0.062	62%	0.111	111%	0.067	67%	0.085	85%	0.074	74%	0.087	87%
Sulprofos	0.065	65%	0.065	65%	0.068	68%	0.107	107%	0.073	73%	0.1	100%	0.078	78%	0.096	96%
Phorate	0.076	76%	0.066	66%	0.086	86%	0.072	72%	0.076	76%	0.079	79%	0.094	94%	0.066	66%
Fonofos	0.06	60%	0.068	68%	0.08	80%	0.074	74%	0.08	80%	0.077	77%	0.096	96%	0.087	87%
Disulfoton	0.074	74%	0.091	91%	0.094	94%	0.088	88%	0.084	84%	0.088	88%	0.095	95%	0.1	100%
Piperonyl butoxide	0.068	68%	0.071	71%	0.076	76%	0.063	63%	0.074	74%	0.07	70%	0.095	95%	0.069	69%
Diazinon	0.063	63%	0.11	110%	0.105	105%	0.08	80%	0.119	119%	0.113	113%	0.112	112%	0.113	113%
Isazophos	0.079	79%	0.093	93%	0.089	89%	0.085	85%	0.083	83%	0.095	95%	0.085	85%	0.081	81%
Chlorpyrifos methyl	0.097	97%	0.08	80%	0.085	85%	0.084	84%	0.069	69%	0.076	76%	0.083	83%	0.081	81%
Pirimiphos methyl	0.099	99%	0.106	106%	0.096	96%	0.108	108%	0.081	81%	0.122	122%	0.12	120%	0.132	132%
Chlorpyrifos	0.075	75%	0.07	70%	0.079	79%	0.083	83%	0.073	73%	0.066	66%	0.079	79		

Figure 2. FMS Inc. Pressurized Extraction System



Conclusions

- High Throughput Pesticide Analysis
- 20 minutes per run up to 24 samples per hour
- Up to 192 samples per 8 hour Shift
- Eliminate Manual Steps and Human Error
- Automated Extraction and Cleanup
- Fast, Consistent, Reproducible Results
- Excellent Recoveries of 203 Pesticides



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