

# Pesticide Analysis for Organic Cut Roses using QuEChERS, GC-MS, and GCxGC-TOFMS

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## Introduction

- Most cut flowers sold in the US are imported from Latin America.
- United States Department of Agriculture (USDA).
  - Regulates only pests and disease on imported flowers.
  - Regulations do not address presence or quantity of pesticides.
- The USDA policy may unintentionally encourage heavy pesticide use on imported flowers.
- Heavy pesticide use has serious consequences for the health of workers in the flower industry, and their local environment.
- Organic or Sustainable Certification
  - Government regulated process - USDA Certified Organic products.
  - Private process - limited use of pesticides and focus on sustainable agricultural practices (e.g. VeriFlora).
- The Quick – Easy – Cheap – Effective – Rugged – Safe (QuEChERS) sample preparation approach was used with GC-MS and GCxGC-TOFMS to analyze pesticides on cut roses.

## Experimental

- Rose leaves and petals were extracted using QuEChERS (Figure 1).
- Method development focused on leaves when GC-MS screening showed higher levels of pesticides compared to petals.



- A 50 pesticides mix was spiked into leaf samples to optimize extraction and GC-MS.
- Water was added to leaves to aid comminution and extraction.
  - 1 g leaves : 4 g water
- Three dispersive solid phase extraction (dSPE) sorbent formulations were evaluated for cleanup efficiency.

25mg PSA	50mg PSA	50mg PSA
7.5mg GCB	50mg GCB	50mg C18
150mg MgSO4	150mg MgSO4	150mg MgSO4

- GC-MS was used to determine presence of target pesticides in VeriFlora-certified and non-certified rose leaf samples.
  - 30m x 0.25mm x 0.25µm Rxi-5Sil MS
  - GC oven: 62.5°C (1 min), 9°C/min to 330°C
  - Inlet: 250°C splitless
  - MS interface: 280°C
  - MS: selected ion monitoring (SIM) mode, quadrupole

- Matrix-matched standards were not used because all rose leaf samples had pesticide residues.

- GCxGC-TOFMS was used to quantify target pesticides and identify non-target pesticides in QuEChERS extracts of rose leaf samples.

- 30m x 0.25mm x 0.25µm Rxi-5Sil MS (primary column)
- Thermal modulation
- 1.5m x 0.18mm x 0.20µm Rtx-200 (secondary column)
- LECO Pegasus 4D TOFMS: EI, 45 to 550u, 100 spectra/sec

## Results

- Based on color (Figure 2), and since planar pesticides are at risk for low recoveries with GCB, 50mg PSA + 50mg of C18 was used for dSPE.
- Table 1 shows GC-MS SIM targeted pesticides (some structures shown in Figure 3) found in VeriFlora and non-certified rose samples.
- Figure 4 shows an orthogonal two-dimensional (GCxGC) separation of pesticides often used on imported roses, achieved by using Rxi-5Sil MS and Rtx-200 columns.
- Tables 2-4 show unbiased GCxGC-TOFMS quantification of targeted pesticides in rose leaf extracts. In addition, non-targeted pesticides are quantified (estimates only) against select target-pesticide calibrations.
- Non-targeted pesticides were found and confirmed through the pg-sensitive, full mass-range capability of the TOFMS (example, Figure 5).

## Conclusions

- The QuEChERS approach was successfully used to determine pesticides with GC-MS (SIM) and GCxGC-TOFMS.
- GCxGC-TOFMS allowed accurate quantification for target pesticides without matrix interference, due to two-dimensional separation.
- VeriFlora-certified roses had a surprising number of pesticides.

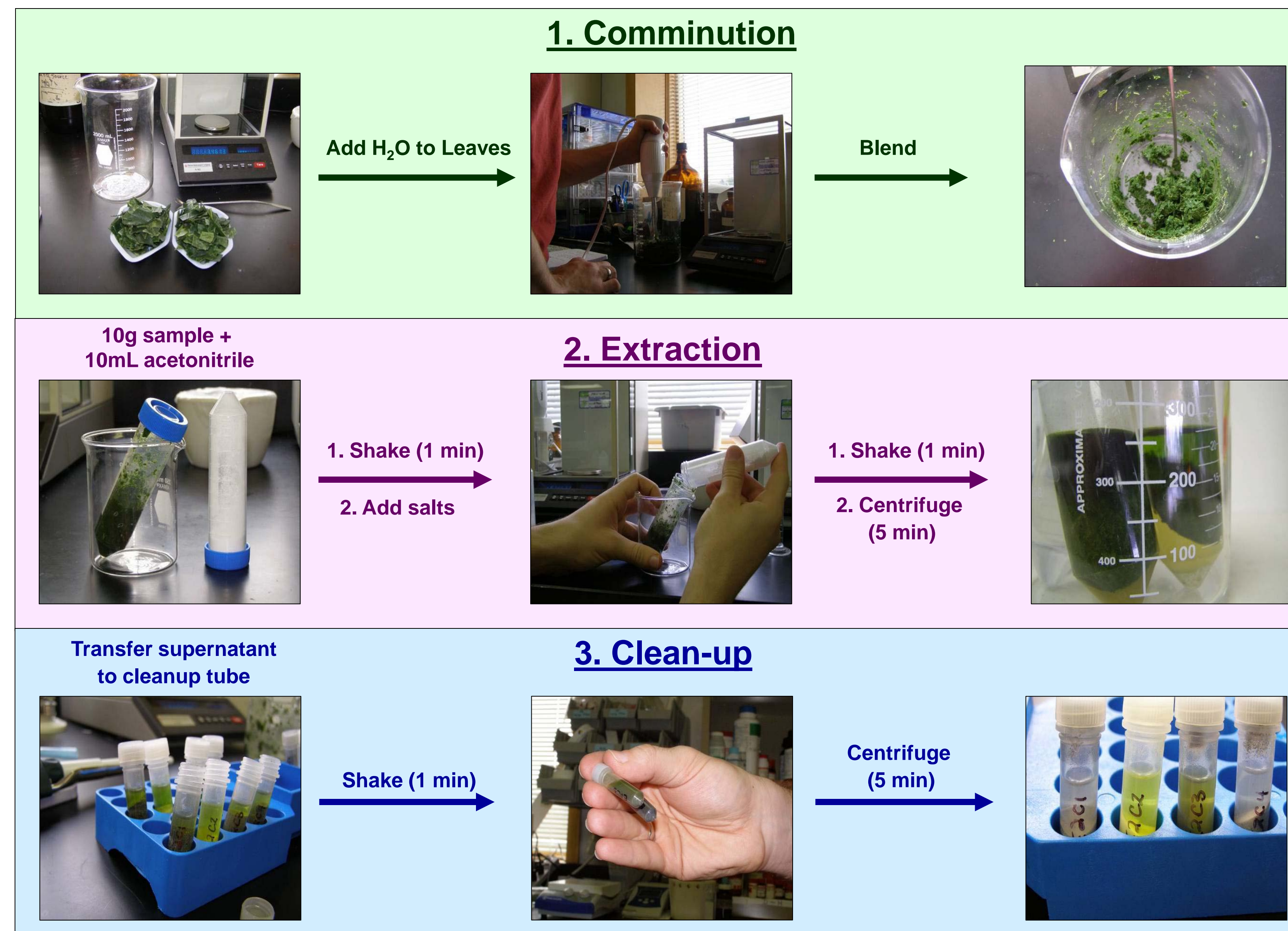


Figure 1. QuEChERS sample preparation for organic-certified and non-certified rose leaves. Three different sorbent formulations were tested during step 3.

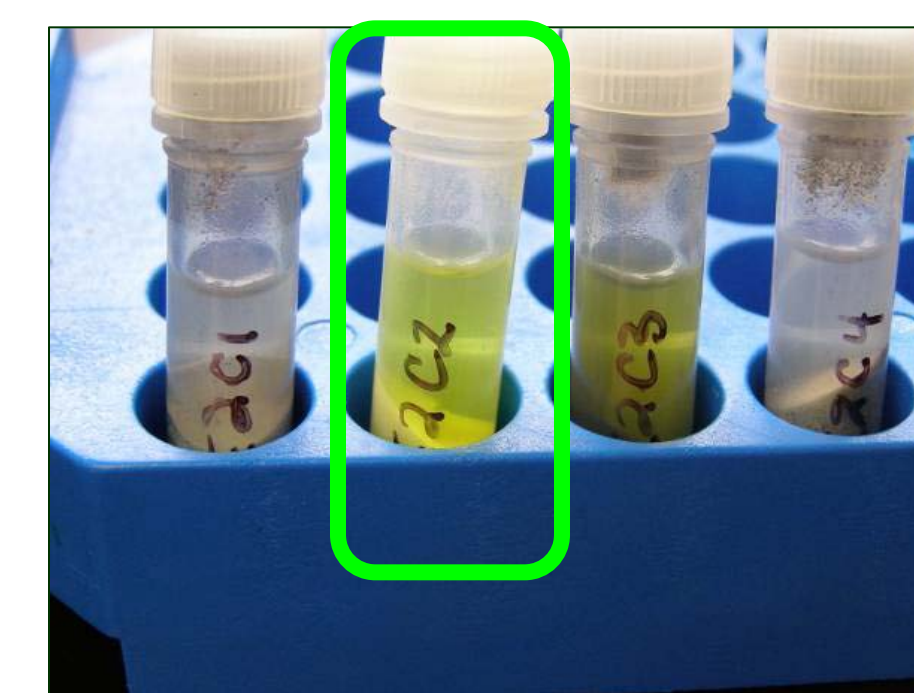


Figure 2. QuEChERS extracts of rose leaves after dSPE. PSA/C18 (50:50) cleanup is highlighted.

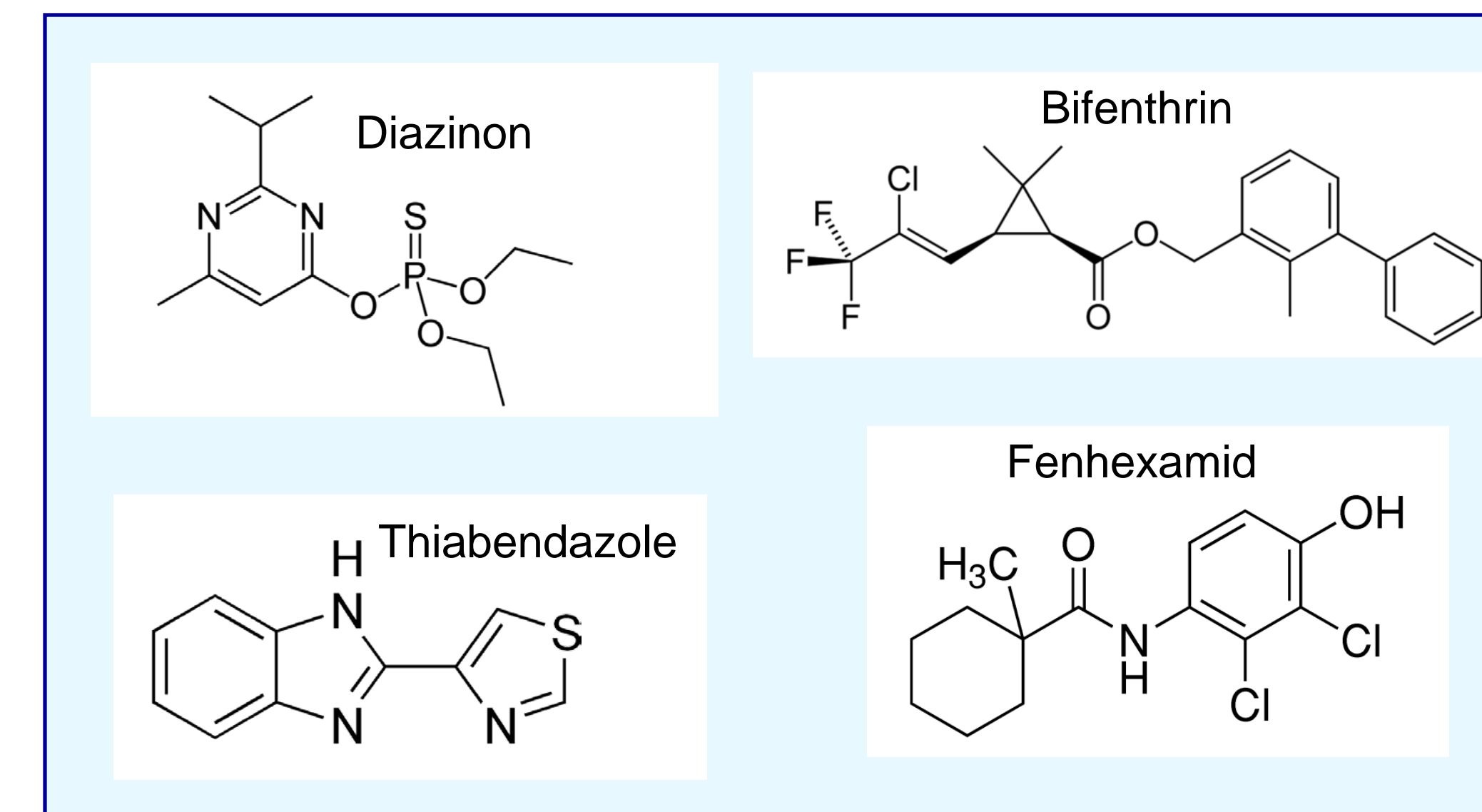


Figure 3. Some pesticides typically found on imported roses.

Table 1. Pesticides detected with GC-MS (SIM) in either or both certified (VeriFlora) and non-certified (local florist) rose leaves QuEChERS extracts.

Name	VeriFlora	Non-certified	Action	Chemical Class
Cyfluthrin	✓		Insecticide	Pyrethroid
Bifenthrin	✓		Insecticide	Pyrethroid
Diazinon	✓		Insecticide	Organophosphorus
Permethrin	✓	✓	Insecticide	Pyrethroid
Thiabendazole	✓	✓	Fungicide	Organonitrogen
Fenhexamid	✓	✓	Fungicide	Organonitrogen
Iprodione	✓	✓	Fungicide	Organonitrogen
Tebuconazole	✓	✓	Fungicide	Organonitrogen
Acephate		✓	Insecticide	Organophosphorus
Cyprodinil		✓	Fungicide	Organonitrogen
Fludioxonil		✓	Fungicide	Organonitrogen
Triadimefon		✓	Fungicide	Organochlorine

Happy Valentine's Day!  
I got you some Thiabendazole, Fenhexamid, Iprodione, and Tebuconazole; and, they're red...

Thanks baby, you know how much I love fungicides!

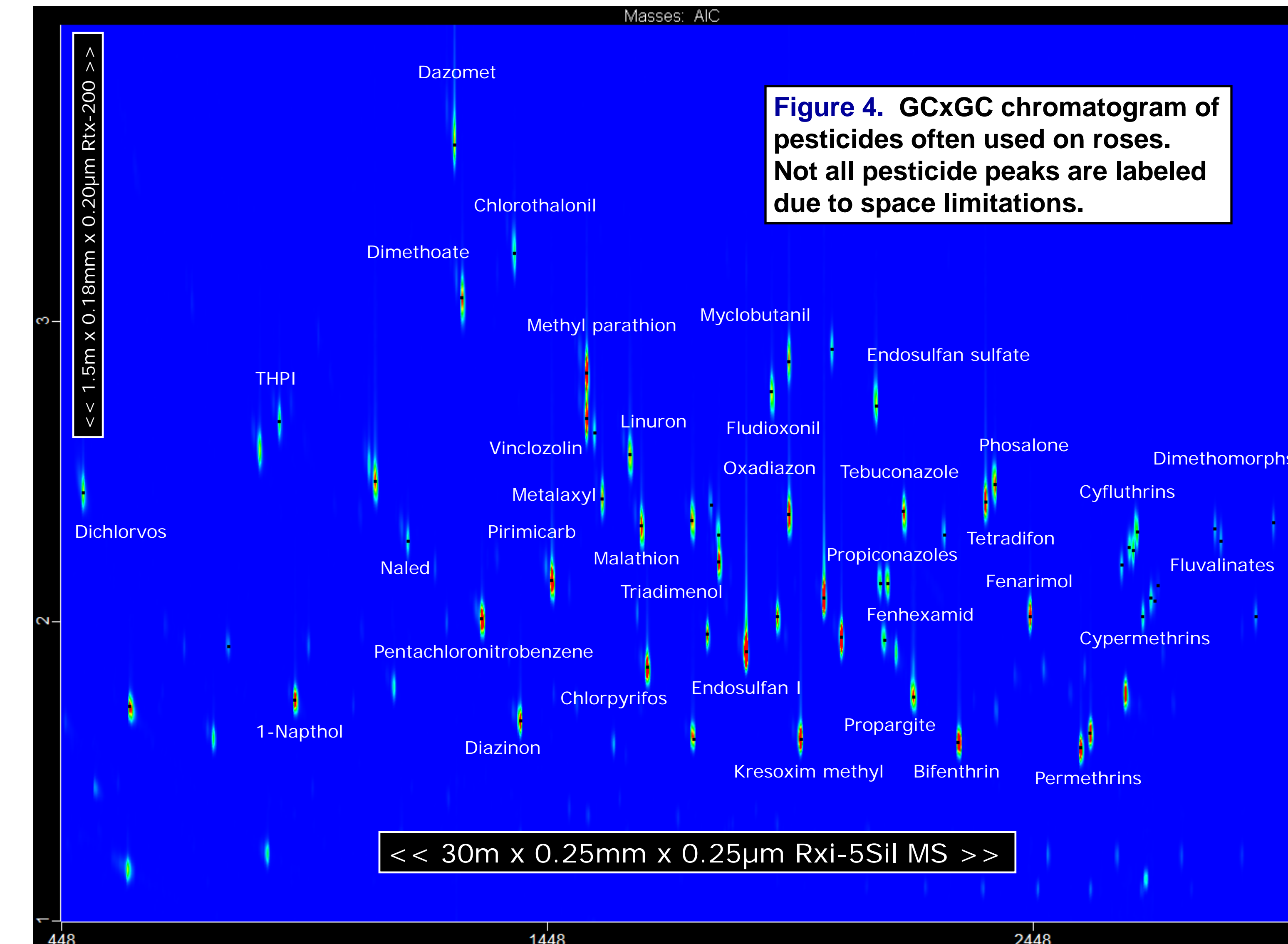


Figure 4. GCxGC chromatogram of pesticides often used on roses. Not all pesticide peaks are labeled due to space limitations.

GCxGC-TOFMS

Table 2. Pesticide amounts on South American non-certified roses (leaves).

Pesticide	Target?	Action	Chemical Class	Q Mass	ppm
Dichloroaniline	Y	Degradation product	Organochlorine	161	0.12
THPI	Y	Degradation product	Organonitrogen	151	13
1-Naphthol	Y	Degradation product	Other	144	0.17
o-Phenylphenol	N	Fungicide	Other	170	2.3
Thiabendazole	Y	Fungicide	Organonitrogen	174	95
Triadimenol	Y	Fungicide	Organonitrogen	168	0.019
Iprodione	Y	Fungicide	Organonitrogen	314	0.22
Bifenazate	N	Acaricide	Organonitrogen	196	0.73
Pyridaben	N	Acaricide	Organonitrogen	147	0.82
Prochloraz	N	Fungicide	Organonitrogen	308	4.4

Table 3. Pesticide amounts on locally-purchased non-certified roses (leaves).

Pesticide	Target?	Action	Chemical Class	Q Mass	ppm
THPI	Y	Degradation product	Organochlorine	151	200
1-Naphthol	Y	Degradation product	Organonitrogen	144	0.030
Pentachlorobenzonitrile	N	Fungicide	Organochlorine	275	0.56
Ethirimol	N	Fungicide	Organonitrogen	166	2.8
Penconazole	N	Fungicide	Organonitrogen	248	0.028
Dodemorph	N	Fungicide	Organonitrogen	154	0.11
Thiabendazole	Y	Fungicide	Organonitrogen	174	2.3
Triadimenol	Y	Fungicide	Organonitrogen	168	0.45
Flutriafol	N	Fungicide	Organonitrogen	219	0.34
Buprofezin	N	Insecticide	Organonitrogen	172	0.055
Tebuconazole	Y	Fungicide	Organonitrogen	250	1.5
Iprodione	Y	Fungicide	Organonitrogen	314	0.34
Cyhalothrin	N	Insecticide	Pyrethroid	181	0.021
Difenoconazole	N	Fungicide	Organonitrogen	265	0.46
Dimethomorph	Y	Fungicide	Organonitrogen	301	0.055

Table 4. Pesticide amounts on VeriFlora-certified roses (leaves).

Pesticide	Target?	Action	Chemical Class	Q Mass	ppm
THPI	Y	Degradation product	Organochlorine	151	0.82
1-Naphthol	Y	Degradation product	Organonitrogen	144	0.045
Dodemorph	N	Fungicide	Organonitrogen	154	0.11
Thiabendazole	Y	Fungicide	Organonitrogen	174	1.4
Imidacloprid	N	Insecticide	Organonitrogen	211	0.032
Fenhexamid	Y	Fungicide	Organonitrogen	177	0.16
Tebuconazole	Y	Fungicide	Organonitrogen	250	1.2
Iprodione	Y	Fungicide	Organonitrogen	314	32
Cyfluthrin	Y	Insecticide	Pyrethroid	163	0.063

Figure 5. Bifenazate found on South American non-certified roses as a non-target pesticide using GCxGC-TOFMS.

