Application Note

# Performance Evaluation of 41 Common Pesticides by LC-SICRIT featuring Shimadzu LC-40 and 9030 LC-MS QToF

## Introduction

Pesticides are amongst the most regulated substances in the world, and due to their widespread use, these compounds continue to be the focus of many routine food and water analytical laboratories. Due to the diversity between different pesticide groups, analysis may have to be completed through different methods, depending on the class of target compounds for analysis. The common coupling methods for analysis are Gas Chromatography (GC) and Liquid Chromatography (GC) Mass Spectrometry (MS), in this case we will focus on LC-MS exclusively. The ionization techniques used with LC-MS or LC-MSMS measurements, are either Atmospheric pressure chemical ionization (APCI) for the more non-polar compounds and Electron spray ionization (ESI) for the more polar compounds. To bridge this gap between the different pesticide analyte classes, and provide a new perspective on LC ionization, we present SICRIT® LC-Module, which takes the advantages of the pre-existing SICRIT® ionization source, conventionally a gas-phase ionization technique, and applies it to an LC method, allowing for soft ionization of both polar and non-polar compounds. This means that only a single ionization source is required to cover the broad spectrum of all standard pesticides. In this study, we utilize a HRMS coupled to the SICRIT® LC-Module to analyze 41 common pesticides.

## Sample Preparation

For calibration, a dilution series of Pesticide Standard Mixes (100ug/mL in ACN; #1, #6, and #8 PN:31971, Restek) were prepared in water ranging from 0.3 ppb to 100 ppb. In total, 41 compounds were analyzed.

*Figure 1: Instrumental setup for this study*

## Analysis Conditions

The SICRIT® technology enables flexible coupling of either gas, liquid, or supercritical fluid chromatographic separation to any LC-MS. Here a Shimadzu LC-40 was interfaced to a Shimadzu 9030 LC-MS via the LC-Module and SICRIT® Ion source with accompanying SC-30 Control unit. All LC and MS settings are outlined in Table 1 and 2.

The SICRIT® LC-Module was set to 400 °C with the SC-30 parameters for voltage set to 1600 V and the frequency set to 45000 Hz. The settings for the various flows pertaining to the LC and MS can be found in the tables below (Table 1&2).

Additionally, the MS had a set scan range of 100-1000 m/z and was set to positive to capture all pesticides of interest.

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## Results from Analysis of Standard Samples

To provide an appropriate overview of our dynamic range and reproducibility of the SICRIT® technology, calibration standards, ranging from 0.3 ppb to 100 ppb, were analyzed in triplicates. In order to summarize our findings effectively, we decided to "showcase" three of the previously stated standards, totaling to 41 pesticides, were detected and were mainly ionized as their $[M+H]^+$ species. This shows that even with a gas-phase technique adapted to a LC method, we are able to consistently produce the $[M+H]^+$ under completely different conditions and methods.

Calibration curves were constructed for each compound providing suitable linearity with correlation coefficients of $(r^2)>0.97$. The calibration ranges and corresponding coefficients of determination $(r^2)$ for 6 of the 41 pesticides are shown in Table 3, with their calibrations can be seen in Figure 2.

| LC - Settings | | |
|---|---|---|
| | **Instrument** | Shimadzu LC-40 |
| | SETTINGS | CONDITIONS |
| | **Column** | |
| | Type | Zorbax Eclipse Plus C18, 50mm x 2.1 mm, 1.8 µm |
| | Guard Column | Phenomenex |
| | Column Oven Temp. | 45°C |
| | **Injection** | |
| | Total Injection Volume (in µL) | 10 |
| | Injection Programm | Co-Injection |
| | Set Injection Volume (in µL) | 2 |
| | **Solvents** | |
| | Flow (mL/min) | 0,3 |
| | Solvent A | 0,1%FA+4mM Ammonium Formate in H2O |
| | Solvent B | MeOH |
| | **Solvent Gradient** | |
| | 0.00 | 10 |
| | 2.00 | 10 |
| | 5.30 | 60 |
| | 10.70 | 70 |
| | 14.70 | 100 |
| | 17.00 | 100 |
| | 17.01 | 10 |
| | 20.00 | 10 |
| | Total Runtime (min) | 20.00 |

*Table 1: LC Parameters*

The reproducibility of 3 replicate injections was measured for each compounds' lowest concentration on the calibration curve, of 0.3 ppb, which was the lowest observable concentration found. A % RSD ≤ 1% for all 41 compounds was achieved for the triplicate injections, showing reliable, reproducible, results at the lowest obtainable concentration for these calibrations. The %RSD for the 6 previously mentioned pesticides can be viewed in Table 3, along with the corresponding lowest observed concentration. It is important to note that these values were obtained and calculated from the results of a Full Scan Mode method and did not require SIMs or MRMs to observe these compounds, even at much lower concentrations.

| MS - Settings | | |
|---|---|---|
| | **Instrument** | Shimadzu 9030 QTOF |
| | **Ion Source** | SICRIT / LC-Module |
| | **MS Tuning Settings** | |
| | Last Tuning | 01.03.2023 |
| | Last Mass Calibration | 01.03.2023 |
| | Tuning File | Tuning_01032023 |
| | **Inlet / Source Conditions** | |
| | Interface Voltage | off |
| | Detector Voltage | 0 kV |
| | Nebulizing Gas Flow | 0.95 L/min (set to 3.0) |
| | Drying Gas Flow | off |
| | Heating Gas Flow | 2.25 L/min (set to 3.0) |
| | Desolvation Line Temp. | 250 °C |
| | Heat Block Temp. | 250 °C |
| | CID Gas Pressure | 150 kPa |
| | **Scan Conditions** | |
| | Scan Mode | Full Scan |
| | Scan Range | 100-1000 m/z |
| | Polarity | + |
| | ID | off |
| | Event Time | 0.100 sec |
| | Save Profile | no |
| | Threshold | low |
| | **SICRIT Conditions** | |
| | Voltage | 1600 V |
| | Frequency | 45000 Hz |
| | Module Temp | 400 °C |
| | Humidifier | no |

*Table 2: MS Parameters*





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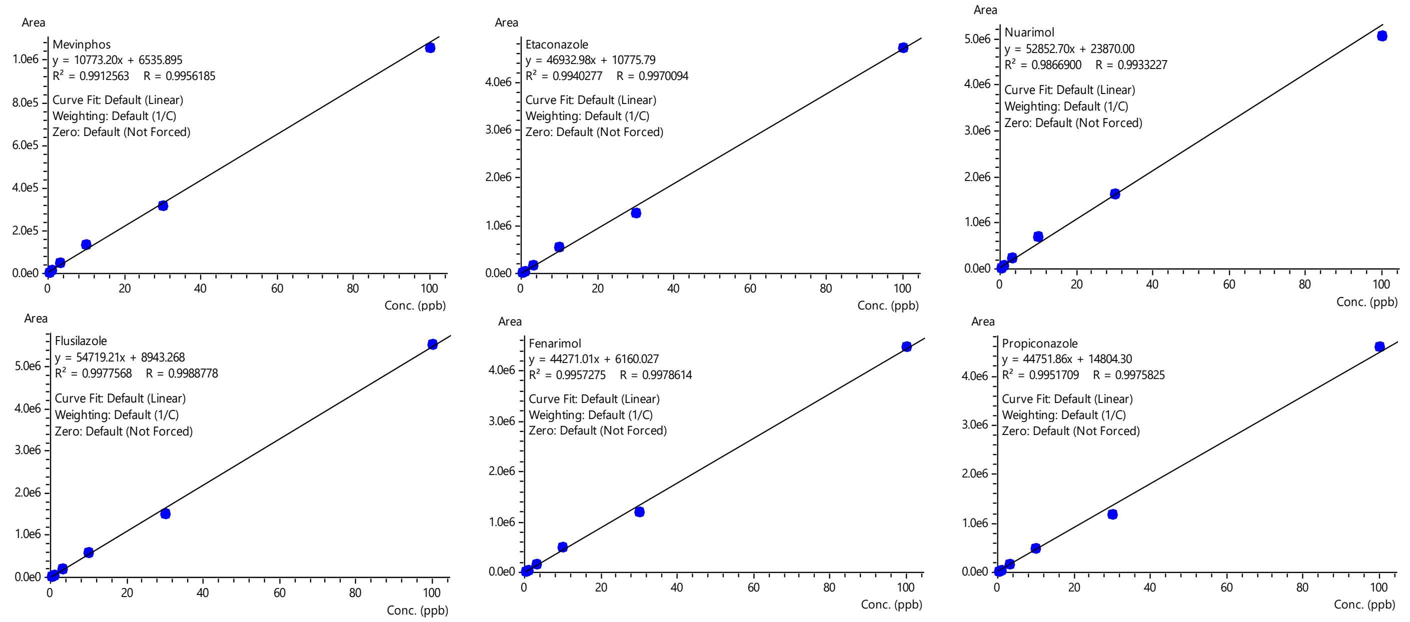


*Figure 2: Calibration curves for Mevinphos, Nuarimol, Fenarimol, Etaconazole, Flusilazole, and Propiconaz*

| Compound | [M+H]+ (m/z) | Retention time (min) | Calibration Curve (ppb) | Correlation Coefficient ($R^2$) | Lowest Conc. Observed (ppb) | S/N (n=3, 0.3 ppb) | Reproducibility (Area %RSD; n = 3; 0.3ppb) |
|---|---|---|---|---|---|---|---|
| Mevinphos | 225.0523 | 5.458 | 0.3 - 100 | 5.61 | 0.3 | 5.61 | 0.04 |
| Nuarimol | 315.0695 | 7.320 | 0.3 - 100 | 24.81 | 0.3 | 24.81 | 0.02 |
| Fenarimol | 331.0399 | 8.292 | 0.3 - 100 | 26.36 | 0.3 | 26.36 | 0.06 |
| Etaconazole | 328.0614 | 8.458 | 0.3 - 100 | 21.20 | 0.3 | 21.20 | 0.02 |
| Flusilazole | 316.1076 | 8.937 | 0.3 - 100 | 13.96 | 0.3 | 13.96 | 0.03 |
| Propiconazole | 342.0771 | 9.748 | 0.3 - 100 | 22.71 | 0.3 | 22.71 | 0.04 |

*Table 3: Summary of the calibration results*

## Conclusion

What this study has been able to provide is further insight into the sensitivity, reproducibility, and versatility of SICRIT® ionization technology. This inherently gas-phase technique has been successfully adapted to work with methods and compound standards, specifically built for ESI, with little to no modification. In addition to the technique being adaptable for LC-MS, we were also able to provide these comparable results using Full Scan Mode, without the need of SIMs or MRMs, which allows for method flexibility and the additional analysis of untargeted components. Furthermore, with these promising findings, we show that the SICRIT® LC-Module is a complementary technique, for both full-scan and MRM experimental set-ups, in the world of pesticide analysis, providing novel ionization mechanisms and reproducible, sensitive results.

## Acknowledgements

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## References

Chromatogramme. Restek. (n.d.). https://www.restek.com/global/de/chromatogram-detail/LC_FF0517

Ganaie, H. A. (2021). Environmental and pesticide pollution. Pesticide Contamination in Freshwater and Soil Environs, 1–20. https://doi.org/10.1201/9781003104957-1





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