# SICRIT® Technology for Fast and Direct SPME-MS Analysis of Environmental Trace Contaminants

## Summary

We present a versatile method for direct and quantitative identification of trace contaminants in environmental samples without sample preparation using SICRIT® soft ionization technology.

## Introduction

The ability to perform a fast and simple trace analysis has become a necessity in numerous fields, such as biomedical, forensic, food, and environmental analysis. In actual High-Throughput Screening (HTS)-applications, LC- and GC-MS methods play a major role in specific and sensitive trace compound analysis. However, tedious sample pretreatment and analyte separation by HPLC or GC present the bottlenecks in fast and simple sample processing.

To overcome this limit in sample throughput, new methods are needed, which simplify and shorten sample pretreatment and quantitative measurement.

Ambient mass spectrometry has been proven to be a versatile tool for fast and direct analysis, requiring minimal or no sample preparation. Our approach to address this demand involves the direct coupling of solid-phase microextraction (SPME) to a very efficient ionization source (SICRIT®, Soft Ionization by Chemical Reaction In Transfer) based on a dielectric barrier discharge (DBD) [1]. Using a PAL RTC system, sample preparation and SPME fiber loading can be automatized and directly combined with MS analysis via Plasmion's SICRIT® ion source.

The advantages of this direct SPME-MS analysis approach are:

- Short sample run times
- High-sensitive flow-through ionization
- High-resolution MS data for identification
- Soft ionization with barely fragmentation
- Extension of analyte range to low polarity

## Experimental Setup

The measurements presented in this publication were performed at ETH Zurich (workgroup of Prof. Zenobi) in collaboration with CTC Analytics AG (Zwingen, CH)

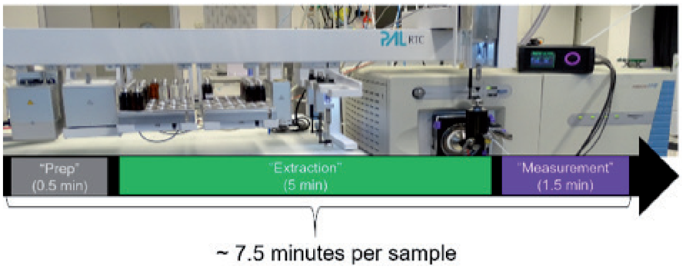

Figure 1 - Experimental setup and worklflow of direct SPME-MS.

Table 1 - Experimental setup and SPME extraction protocol.

| | |
|---|---|
| Samples | Analytical standards (Sigma-Aldrich),<br>1 mg/mL methanolic stock solutions |
| Solvent | MS-grade solvents (Sigma-Aldrich) |
| Mass spectrometer | LTQ Orbitrap (Thermo Fisher) |
| SICRIT Plasma | 1.5 kV, 10 kHz |
| Automatized Sampling | PAL RTC (CTC Analytics) |
| SPME | DVB/PDMS arrow (CTC Analytics) |
| SPME extraction | 5 min, 1500 rpm stirring, 40°C |
| SPME desorption | 1.5 min, 260°C |
| Split ratio | 1:10 |
| Carrier gas | Humified $N_2$ (90% R.H. |

## Results

The investigation of direct SPME-MS coupling by means of Plasmion's soft ionization source included various polar and non-polar analytes in different matrices to evaluate the potential of this approach for fast and quantitative HTS screening.
In particular, the analysis of polycyclic aromatic hydrocarbons (PAH) in water samples was evaluated. For these non-polar analytes, standard MS-ionization techniques (ESI, APCI) lack in sensitivity and require lengthy liquid chromatography.

An ionization source also enabling for detection of low-polarity analytes would enlarge the scope of applications that becomes accessible with plasma-based ionization. The results of these studies can be obtained in detail from literature.[2]

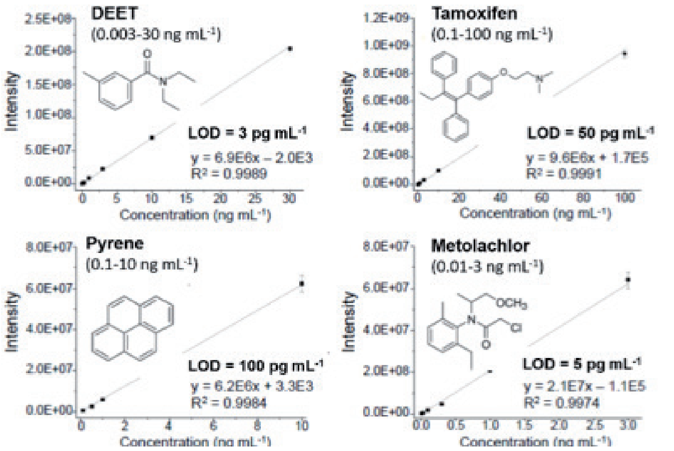

Figure 2 - Calibration curves for DEET, Tamoxifen, Pyrene, and Metolachlor in water, obtained with direct SPME-SICRIT®-MS.[2]

To sum up the results, successful ionization of PAHs (according to CRM47930 PAH mix) could be performed with SICRIT®. In view of sensitivity, it could be demonstrated, that addition of dopants increases the ionization efficiency and thus sensitivity significantly. Using fluorobenzene as solvent, LODs in the ppt-range could be revealed.[2]
In Figure 2, calibration curves of four known contaminants in water are depicted, which are covering varying polarities. Using an SPME extraction and desorption protocol with run times of about 8 minutes, the data show excellent linearity ($R^2 > 0.99$) and LODs in the ppt-range for all substances. Comparing with literature, these LODs point up the competitiveness of the direct SPME-MS approach for fast HTS purposes.

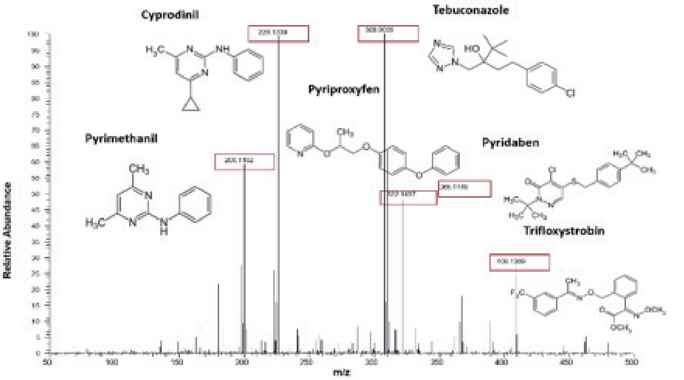

Figure 3 - HRMS full scan of a soil sample spiked with pesticides.

Furthermore, SPME coupling with high-resolution MS systems (HRMS) is a versatile new tool for non-target screening of environmental samples as exemplarily shown in Figure 3. Here, a soil sample was spiked with pesticides and analysed, showing the ionization of compounds with higher polarities.
The use of a PAL RTC autosampler allows automated sample processing, with virtually no manual preparation steps.

A proof of concept of SPME-SICRIT-MS for foodstuff and forensic analysis was also performed. Therefore, different food samples, e.g. fruit and fruit juices, were prepared and extracted with SPME arrows. In Figure 4, calibration of the insecticide sulfotep in apple matrix is shown. The LOD was calculated to 80 ng/L. These data suggest rapid and quantitative analysis of complex food samples.

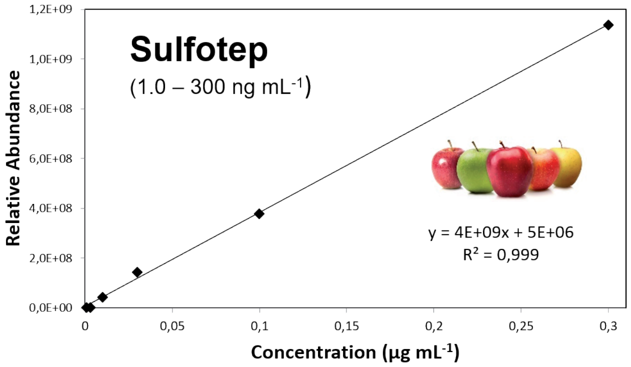

Figure 4 - Calibration curve of sulfotep in apple samples, obtained with direct, obtained with direct SPME-SICRIT®-MS.

## Conclusions

The presented data show the potential of direct SPME-MS using Plasmion's SICRIT® ion source technology for rapid HTS screening purposes. The broad polarity range of analytes, the quantitative and sensitive detection, and the combinability with PAL autosampler systems prove the SICRIT approach as a promising new technology for target and non-target trace analysis on any LC-MS instrument.

## References

[1] M.F. Mirabelli, J.-C.Wolf, R. Zenobi, Anal. Chem. 2016, 88, 7752-7758.
[2] A.K. Huba, M.F. Mirabelli, R. Zenobi, Anal. Chim. Acta, 2018, 1030, 125-132.