



Water

## Easy catch: pesticides

Pesticides in water are easy to catch i.e. extract, but often an additional analyte concentration step is required in order to meet the limits of detection (LODs) specified in rules and regulations. A complete automated sample preparation system consisting of a GERSTEL MultiPurpose Sampler (MPS) with SPE option and a solvent evaporation station was put to the test in the work described here. System performance, including automated extraction, was tested for 18 pesticides at the 10 ng/L level in groundwater. The analytes were extracted, concentrated, and determined using LC-MS/MS. Performance criteria were ruggedness, recovery of analytes, method linearity and sample to sample reproducibility.

The pesticides appear to have taken the bait.

Having to reach ever lower limits of detection (LODs) is a daily challenge in modern laboratories. In order to succeed in obtaining sufficiently sensitive analysis methods, sample preparation techniques such as Solid Phase Extraction (SPE) or Liquid-Liquid Extraction (LLE) are often used as combined extraction and concentration steps. The concentration factor achieved in these cases depends on the ratio between the extracted sample volume and the amount of solvent used for analyte elution from the SPE cartridge or for liquid extraction. Following the extraction, a further evaporative concentration step can be performed, significantly improving the limits of detection for the overall analytical method. For example, an extra concentration step can help to meet the requirements of the

water EU framework directive 2008/105/EC for pesticides in ground and drinking water.

For the evaporative concentration step, semi-automated solutions are widely used, in which a number of samples are concentrated under a flow of nitrogen at a moderately increased temperature. In such systems, sample transfer is handled manually. The GERSTEL MultiPosition Evaporation Station (mVAP) in combination with the GERSTEL MultiPurpose Sampler (MPS) now offers fully automated concentration of sample extracts.

The system enables complete automation of all sample preparation steps including introduction to the LC- or GC-system. The evaporation is controlled by controlling the applied vacuum, tem-

### Manual Sample Preparation

- Sample filtration
- Transfer of filtrate to 25 mL Vial

### SPE Process

- 20 mL sample/filtrate added to cartridge
- SPE Cartridges: M & N C18ec
- Elution with 2 mL MeOH (Concentration 10:1)

### mVap Evaporation

- Evaporation time: 30 min
- Temperature: 60 °C
- Pressure: 200 mbar
- Agitation: 600 rpm
- Evaporation to dryness

### mVap Reconstitution

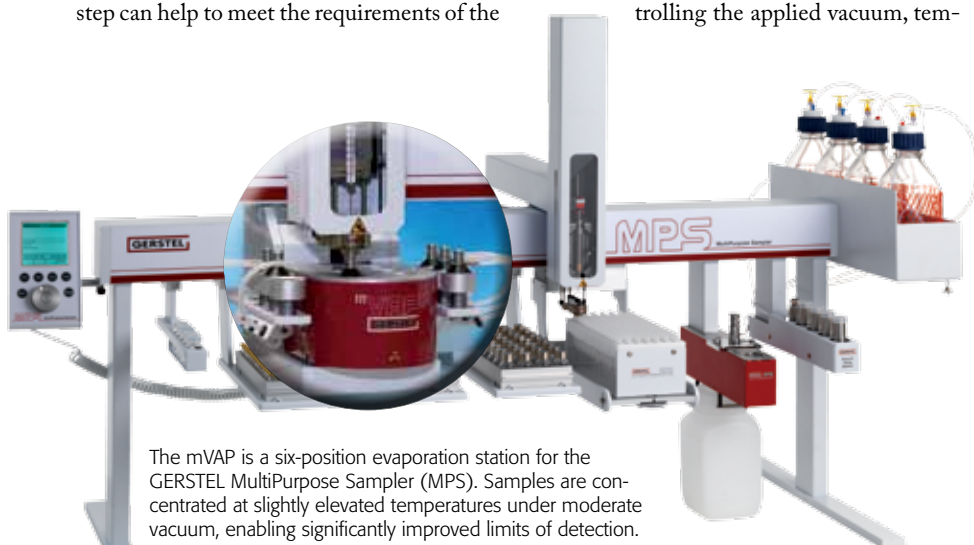
- Addition of 0.5 mL H<sub>2</sub>O
- Incubation time 5 min
- Shaking: 600 rpm

### Transfer to LC-MS/MS

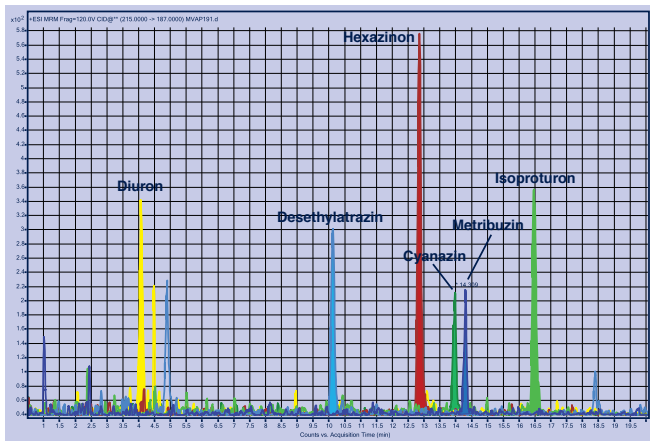
- Transfer of concentrate to 1.5 mL vials
- Analysis with LC-MS/MS

Automated sample preparation process used for the analysis work performed.

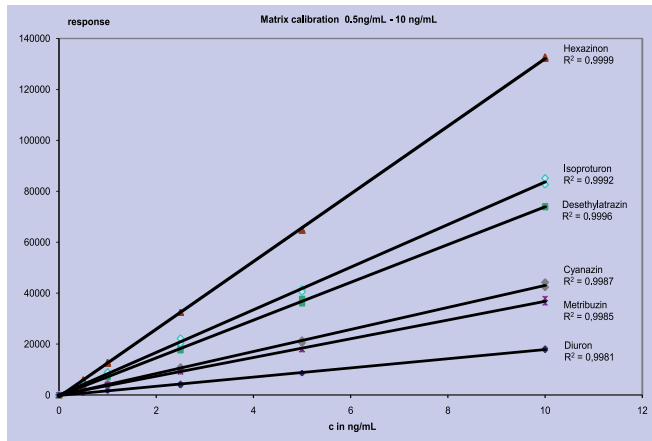
GERSTEL Multi Purpose Sampler MPS with automated Solid Phase Extraction (SPE) and evaporation module mVap.



The mVAP is a six-position evaporation station for the GERSTEL MultiPurpose Sampler (MPS). Samples are concentrated at slightly elevated temperatures under moderate vacuum, enabling significantly improved limits of detection.



Overlay chromatogramm of quantifier MRMs for six selected pesticides extracted from a spiked sample at 10 ppb.



Matrix calibration curves for six selected analytes extracted from spiked groundwater sample.

perature, and agitation leading to reproducible results independent of the solvent used. The user can also benefit from a real increase in laboratory efficiency, since batches of samples can be processed automatically overnight. In this work, the performance of the complete system including the mVAP is demonstrated.

### Experimental

SPE extraction and clean-up was performed using a GERSTEL MultiPurpose Sampler (MPS) fitted with SPE option. Eluate concentration was performed using the GERSTEL MultiPosition evaporation station (mVAP) under MAESTRO software control. LC-MS/MS analysis work was performed using an Agilent 1290 LC system coupled to an Agilent 6490 Triple Quadrupole Mass Spectrometer.

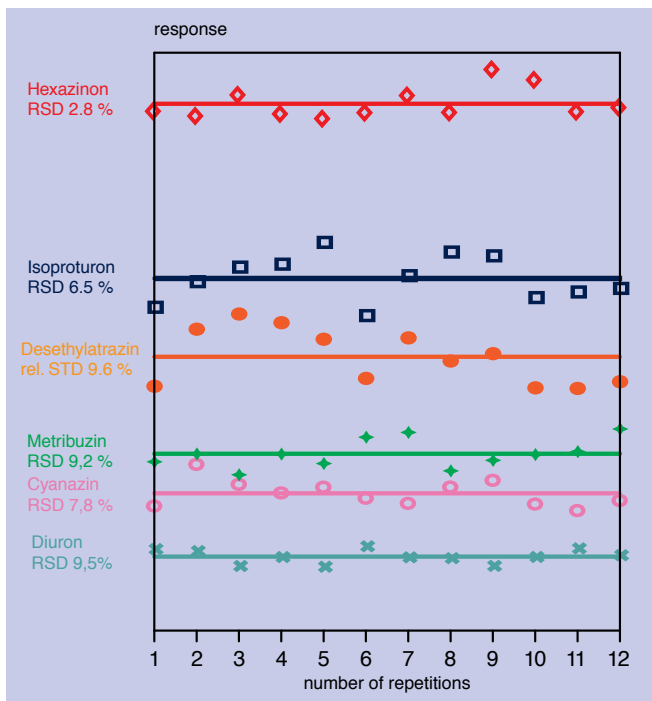
In the mVAP, samples were concentrated at slightly elevated temperatures under moderate vacuum, enabling significantly improved limits of detection. Method parameters are listed in the table to the left.

Spiked groundwater samples were used for matrix calibration and analysis.

### Conclusions

A completely automated process involving SPE and an evaporation step was tested for ruggedness, recovery of analytes, method linearity and sample to sample reproducibility. Data obtained using the mVAP to concentrate extracts containing 18 selected pesticides from groundwater samples clearly demonstrates that the system delivers the required analytical performance while requiring almost no manual handling steps. Calibration curves, sample to sample reproducibility, and recovery rates for the analytes selected, demonstrate the applicability for routine laboratory work.

The GERSTEL MPS with SPE and mVap in combination with an LC-MS/MS system is a powerful tool for determining pesticides in water at low concentration levels.



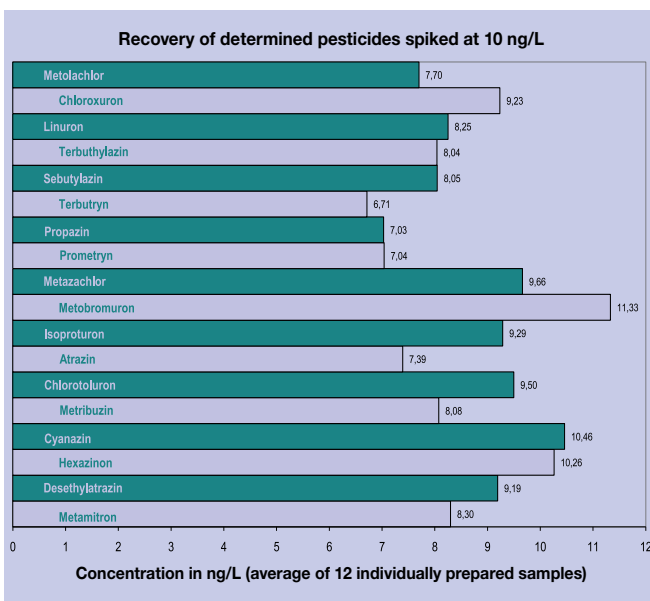
Signal responses and standard deviations for selected analytes from twelve consecutive extractions and analyte determinations.

### References

Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water Policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC and 86/280/EEC, and amending Directive 2000/60/EC, of the European Parliament and the Council.

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The determined 18 pesticides with recoveries.