

## Off-Line SFE-NMR Analysis of DDT in Soil Samples

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### Introduction

Nuclear Magnetic Resonance Spectroscopy (NMR) is a well established technique for structure characterizations, while the use of NMR in environmental analysis has seen limited application due to low sensitivity.

The supercritical fluid extraction (SFE) technique has been exploited for quantitative extraction of organic compounds such as pesticides, from a variety of environmental matrices [1, 2]. The selectivity in the SFE process offers considerable advantages, such as the production of cleaner extracts compared to liquid solvent extracts, which frequently contain large amounts of matrix organics. This reduces the need for cleanup and facilitates quantification of target analytes. SFE can also be used for fractionation of a sample by varying the extraction conditions.

The aim of this investigation was to study off-line SFE-NMR as a method for qualitative analysis of environmental samples. Soil was used as the test matrix, and its content of DDT and metabolites were studied. The results were compared with a conventional solvent extraction (SE) followed by GC analysis.

### Materials and Methods

A native soil sample contaminated with DDT was used in this study. DDT and metabolites (1. o,p'-DDD, 2. p,p'-DDD, 3. o,p'-DDE, 4. p,p'-DDE, 5. o,p'-DDT, 6. p,p'-DDT, Dr Ehrenstorfer, GmbH) in acetone were used as reference standards. All chemicals and standards were used as purchased without further purification.

### *SFE*

An ISCO SFE System 2200 (Lincoln, NE,) was used for the SFE. A 5g soil sample was extracted with carbon dioxide at 55 °C and 285 atm (density 0.85 g/mL), with the addition of methanol as modifier (200 µL, added directly to thimble prior to extraction), using five minutes of static extraction followed by extraction with 20 mL carbon dioxide in the dynamic mode. Analytes were collected in vials, containing acetone.

### *NMR*

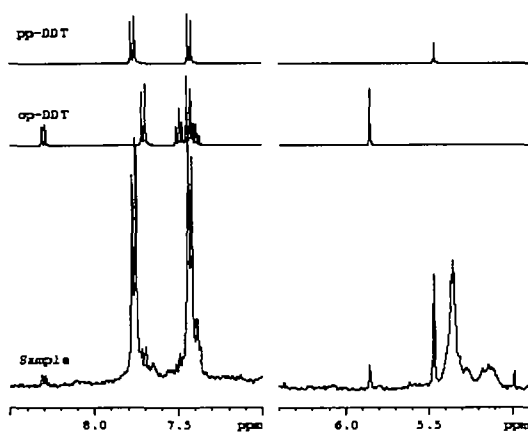
Both the samples and reference compounds were prepared in the same way. The original solvent, acetone, was evaporated and 0.7 mL of deuterated acetone was added (acetone-D<sub>6</sub>, Cambridge Isotope Laboratories, 99.9%). Samples and references were then transferred to NMR-tubes and analysed with a 400 MHz Bruker DRX instrument. Standard 1D <sup>1</sup>H-spectra were acquired at 300°K. The number of scans was 128 for the references and 768 for the sample. The FID's were exponentially multiplied with a line broadening factor of 0.3 Hz before Fourier transformation.

### *GC analysis*

Off-line gas chromatographic analysis of the soil extracts were performed on a Hewlett-Packard 5890 gas chromatograph (Wilmington, DE) equipped with dual columns in conjunction with electron capture detectors.

## **Results and Discussion**

o,p'-DDT and p,p'-DDT were detected in the soil sample after SFE and NMR analysis, while p,p'-DDD and p,p'-DDE could not be detected due to low sensitivity and overlapping by o,p'-DDT and p,p'-DDT signals (Figure 1). Four DDT metabolites were found in the soil sample after SE and GC analysis, p,p'-DDD, p,p'-DDE, o,p'-DDT and p,p'-DDT were detected at approximately 2, 1, 2 and 7 mg/kg respectively.



**Figure 1.**  $^1\text{H}$ -NMR spectrum of soil extract containing DDT metabolites.

The results obtained in this study indicate that the NMR technique can be used for characterization of DDT in environmental analysis, although introduction of NMR instruments with higher sensitivities are needed to gain the full potential of the NMR technique. Such instruments are under way and may turn out to be a powerful tool in the future. The whole sample is analysed with NMR, in comparison with GC where only a small fraction of the sample is analysed, thus, reducing the difference in sensitivity between GC and NMR. Further studies regarding other substances and matrices are needed to evaluate the potential of the described application. Other environmental applications include the use of NMR as a detector-system in chromatography, possibly on-line with a fractionation step such as SFE.

#### References

1. Barnabas, I. J., Dean, J. R. and Owen, S. P; *Analyst*, **119**, 2381-2394 (1994).
2. Böwadt S. and Hawthorne, S. B; *J. Chromatogr. A* **703**: 549-571, (1995).

