# MATRIX SOLID-PHASE DISPERSION ISOLATION AND LIQUID-CHROMATOGRAPHIC DETERMINATION OF METHOMYL IN BIOLOGICAL TISSUES

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**ABSTRACT:** The isolation of methomyl based on matrix solid phase dispersion (MSPD) technique. By blending tissues with bulk octadecylsilyl-derivatised silica we are obtained a semi-dry material which can be used as a column packing material. Than we could elute the methomyl and analysed it by HPLC-DAD.

**KEY WORDS:** Carbamate; Methomyl; HPLC-DAD.

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## INTRODUCTION

Methomyl, (S-methyl-N-([methylcarbamoyl]-oxythio-acetimidate) registered name Lannate® has been developed by E. I. du Pont de Nemours and Company, Incorporated.

Lannate® is widely used as insecticide in agriculture. Suicides and accidents due to carbamate poisoning are occasionally encountered in forensic science practice.

Methomyl toxicity: $LD_{50}$ is orally in male rats – 17 mg/kg, in female rats – 24 mg/kg.

The present paper deals with isolation of methomyl from biological samples by matrix solid phase dispersion (MSPD). The isolation of pesticide from tissue is often a complex and laborious task. Classical methods have approached in general the isolation of pesticide from this matrix different manner: homogenisation, deproteinisation, extraction by organic solvent etc.

We present here a new approach to the isolation of methomyl from biological tissues that appears to eliminate many of these difficulties. The new procedure known as MSPD was developed by researchers at Louisiana State University's School for Veterinary Medicine.

MSPD is an isolation technique using 1 g or less than 1 g of sample and low volumes of solvents. The technique involves homogenisation of a small amount of sample tissue with bulk bonded silica based sorbent in a pestle and mortal. The mechanical shearing forces produced by the grinding process disrupt the structure of the tissue, dispersing the sample over the surface of the support sorbent by hydrophilic and hydrophobic interaction. The process produce a semi-dry and homogenous blend of sample. The

blend is then transferred into a pre-fritted SPE cartridge and elution of interference compounds and analytes of interest.

## EXPERIMENTAL

### Materials

Methomyl analytical 99,80% were obtained from Du Pont de Nemours International S. A. Liquid chromatographic grade solvents were used. Bulk octadecylsilane derivatised silica and Florisil was washed with hexane and methanol and was air dried before using.

### MSPD isolation

0,250 g tissues or spiked tissues were added to 1,0 g of $C_{18}$ packing material in a glass mortal. The sample was gently blended with a glass pestle for 30 s. The semi-dry material was transferred into a pre-fritted SPE column containing 0,150 g of Florisil at the bottom. The column was lightly tamped to remove air pockets, washed with 2 x 2 ml of hexane and vacuum dried. The methomyl was eluted with 2 x 2,5 ml of methanol. The MSPD process is illustrated in Figure 1.

### Analytical procedure

Chromatography was performed with an automated HPLC system consisting of a LC-10AD Shimadzu model with SPD-M10A Diodearray detector. U. V. detection was

Fig. 1. The MSPD process.

operated at 240 nm. Samples were chromatographed on a 250 x 4 mm column packed with LiChrospher 100 RP-18 5 μm material. The mobile phase consisted of acetonitril and water 20:80. The flow rate was 1 ml/min. The injected volume was 20 μl.

**Case history**

36 year old man was lying dead in his garden, besides him a Coca-Cola bottle was found which was contained blue coloured solution. During the toxicological analyses

Fig. 2. Shows the methomyl calibration under these chromatographic parameters.

we identified methomyl from the bottle.

The methomyl concentration found in blood and in tissues of the man are shown in Table I.

TABLE I. THE METHOMYL CONCENTRATION IN POST-MORTEM MATERIAL IN THE CASE OF FATAL POISONING

| Material | Concentration of methomyl [μg/g] |
|---|---|
| Blood | 9 |
| Liver | 21 |
| Kidney | 19 |
| Spleen | 18 |
| Stomach and contents | 104 |

The recovery: 0.250 g liver samples were spiked with 1 μg of methomyl. After this procedure the recovery of methomyl was 70.3% ± 6 (n = 5).

The chromatograms of post-mortem blood sample and spiked liver sample are shown in Figure 3 and Figure 4.

Fig. 3. Chromatogram of methonyl in blood sample.

Figure 4. Chromatogram of methonyl in liver sample.

## CONCLUSION

MSPD isolation have shown to be an efficient, rapid isolation method to examine methomyl in post-mortem tissues. The detection limit of methomyl on the HPLC chromatograms was 2 ng/ml.

The procedure significantly reduced solvent consumption and waste; for this reason the cost of analysis is decreased.

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