A RAPID METHOD TO DETERMINE 1,3-DICHLOROPROPENE (1,3-D) BY GAS CHROMATOGRAPHY ION TRAP MASS SPECTROMETRY ON FRUITS AND VEGETABLES.

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INTRODUCTION

1,3 -Dichloropropene (1,3-D) is an organochlorine compound. It exists either as cis (Z) and trans (E) isomeric form and the two isomers have similar but not identical properties. It is used as a fumigant in the racemic formulations to control nematodes and fungi. It is used by direct injection in the soil or sprayed on the ground and hence released directly to the environment.

Several authors have been described the toxicological properties and the analytical method to determine the concentration of the isomers in the biological fluid of animal due to their toxicological properties, in water and soil due to their environmental properties and environmental and biological monitoring has been described for non-occupational exposure to 1,3-D.

The use of 1,3D as fumigant on fruits and vegetables in the EU is not allowed due to their toxicological properties. (EFSA journal 2009, 7; 10, 1341) . Sensitive and reliable analytical method are required to monitor 1,3-D residues in fruit and vegetable crops. Some authors describe analytical methods on environmental samples (water and soil) but no analytical methods are described for the food samples. Due to the relatively low boiling points and high vapor pressure of the cis and trans isomers, the gas chromatography with electron capture detector (ECD) and mass spectrometry (MS) is more appropriate as determination technique.

ANALYTICAL METHOD

Preparation of extraction solution

Weight approximately 0.1 g of 2-bromo-1-chloropropane (I. S.) into a 50 mL volumetric flask containing approximately 20 mL of hexane. Dilute to volume with hexane to obtain a 2 mg/mL stock solution. Prepare a diluted solution 0.2 mg/mL in hexane and use this solution to prepare calibration solution and extraction solution.

Sample extraction

Weight approximately 10g of homogenized samples into a 50 mL vial. Immediately add 10 mL of the extraction solution containing ISTD. Seal the vial with a PTFE lined closure. Shake mechanically for 15 minutes. Centrifuge the samples at 2500 rpm for 5 minutes. A portion of the organic layer was transferred into an autosampler vial and analyse into GC/MS.

INSTRUMENTAL CONDITIONS

A Varian System Gas Chromatography equipped with a Varian ion trap spectrometry was used. The chromatographic analysis was performed using a DB-VRX column (30 m x 0.25 mm ID, 1.4 µm ft).

The oven temperature started at 25°C (1 min); 35°C to 130°C at 10°C/min; from 130°C to 220°C at 60°C/min held to 220°C for 1 min.

Injector Temperature: 200°C; Interface temperature: 230°C; Carrier gas Helium 42 kPa; Injector mode: splitless, Purge delay: 0.9 minutes, splitless flow: 35 mL/min; Septum purge: 1.0 mL/min; Injection volume: 1 µL

For the quantitative determination the most abundant ions were used:

cis and trans 1,3-D: ion 75 m/z (quantitation) 110 m/z and 112 m/z (confirmatory ion).

Internal Standard ion : 77 m/z.

Figure 1— Total Ion Chromatogram (TIC) of an apple recovery at 0.5 mg/kg spiked level.

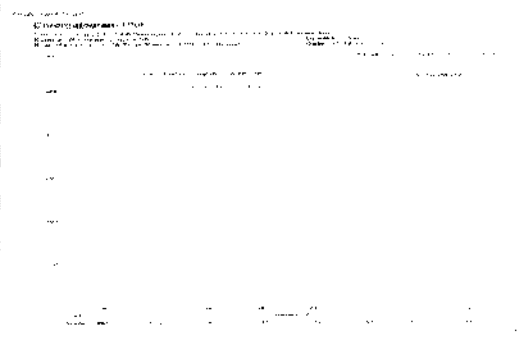

Table 1—Recoveries mean, standard deviation (S.D.) and variation coefficient (RSD%) at 0.05 mg/kg and 0.5 mg/kg spiked levels.

Crops	Compounds	Spiked levels (mg/kg)	
		0.05 mg/kg	0.5 mg/kg
Apple	Cis 1,3D Trans 1,3D	106 ± 10; 9 93 ± 7; 8	88 ± 4; 5 89 ± 7; 8
		0.05 mg/kg	0.5 mg/kg
Lettuce	Cis 1,3D Trans 1,3D	93 ± 13; 14 84 ± 12; 14	108 ± 8; 7 107 ± 14; 13
		0.05 mg/kg	5 mg/kg
Grape	Cis 1,3D Trans 1,3D	76 ± 4; 5 82 ± 5; 6	90 ± 9; 10 91 ± 12; 13

Table 2 - Recoveries of cis and trans 1,3-D at 0.01 mg/kg spiked level (LOQ)

Compounds	Apple	Lettuce	Grape
Cis 1,3-D	86 ± 5; 6	98 ± 8; 9	82 ± 8; 10
Trans 1,3-D	75 ± 10; 13	86 ± 10; 12	99 ± 12; 12

RESULTS AND CONCLUSION

To test the performance of the method the accuracy, precision (repeatability), linearity and limit of determination (LOQ) were determined.

The accuracy of the method was determined by recoveries at two spiked levels 0.05 mg/kg and 0.5 mg/Kg with 5 replicates for each level. For all matrices the mean recoveries were ranged between 76.0 and 108.0% with correlation coefficient (RSD) ranging from 5% to 15% as showed in table 1.

The repeatability was expressed as standard deviation of 5 replicates performed by the same operator, with the same instrument and in the same day. Good repeatability was obtained for all matrices as showed in table 1.

Good linearity ($r2 > 0.99$) was obtained in the concentration range of 0.01 — 0.5 mg/kg in solvent.

The LOQ was calculated as the lowest concentration that can be quantified with acceptable accuracy and precision. The LOQ value is 0.01 mg/kg for each combination active substances/crop.

The method can be considered useful for the routine analysis of 1,3-D on fruit and vegetable crops.