# Analysis of fumigants by GC/MS/MS

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## 1. INTRODUCTION

Fumigants are very volatile and/or gaseous pesticides used for the disinfestation or preservation of foodstuffs, mainly cereals, seeds, and dried fruits.
Most fumigants are not approved in the European Union with a default MRL value of 0.01 mg/kg, but some of these are used outside Europe and as solvents in industry worldwide then it is not unusual to find them as environmental contaminants.
Fumigants can be analyzed with a variety of different approaches, one of the most common being by Head Space Gas Chromatography with mass spectrometry or selective detection (e.g. ECD for halogenated compounds).
Quechers method, now widely used as EN 15662:2018 Standard Method, describes a series of procedures for multiresidual analysis of pesticides by acetonitrile extraction, simple clean up and analysis by chromatography (GC or LC) coupled with mass spectrometry.
The method does not refer to fumigants and the instrumental conditions given by way of example are not suitable for the analysis of highly volatile compounds such as fumigants. In this work we wanted to test the Quechers extraction for the analysis of a series of target fumigants by adapting and optimizing the instrumental conditions to the particular nature of these pesticides.

## 2. EXPERIMENTAL PART

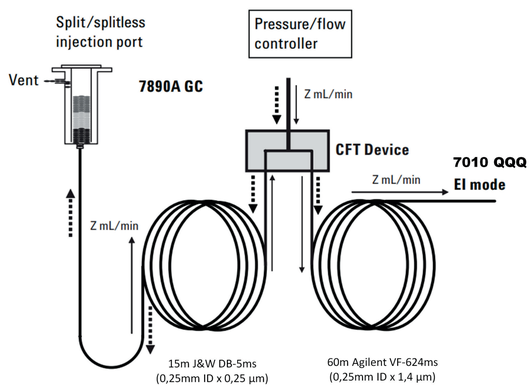
### Sample preparation

In order to avoid analyte losses following the heating of the sample during the grinding and homogenization phase, the sample is weighed intact in PP tubes together with ceramic balls.
Water and acetonitrile are added according E5/E7 procedure of the method and the sample is processed by high-speed bead mill homogenizer.
The salts of step 1 (mixture of anhydrous $MgSO_4$, NaCl and citrate buffer) are added, then the homogenization proceeds followed by the centrifugation and the collection of the organic phase.
The sample is then purified by the C4 procedure (dSPE with PSA/ $MgSO_4$/ODS mix).

### Instrumental analysis

GC Set-up
The hot split technique is used for sample injection.
For this analysis it is used a double column configuration with an auxiliary EPC (pressure control module) as shown in the figure.

*Figura 1*




The pressure is initially set via the injector, while the EPC keeps the flow constant in the second column.
The volatile analytes reach the second column in a few minutes and while the high boiling components are still in the first column the pressure in the inlet is lowered.
The carrier from the auxiliary EPC completes the separation of the volatile components in the second column while the high boiling analytes flow out of the inlet.
In this way, contamination of the analysis column and dirtying the source of the spectrometer are avoided preserving the performance of the system.

*Mass spectrometer Settings*
Fumigants have masses on average lower than those of semi-volatile pesticides, therefore MRM conditions must be optimized with particular care to avoid interference from fragments of other molecules and / or gases present in the ambient air.
For this analysis, 3 MRM transitions were optimized for each analyte.

Compound Table *Tabella 1*

| Compound Name | RT | Precursor Ion | Product Ion | CE |
|---|---|---|---|---|
| Carbon Tetrachloride | 13,0 | 121 | 84 | 40 |
| Carbon Tetrachloride | 13,0 | 119 | 84 | 40 |
| Carbon Tetrachloride | 13,0 | 119 | 82 | 40 |
| 1,2-Dichloroethane | 13,8 | 100 | 64 | 5 |
| 1,2-Dichloroethane | 13,8 | 64 | 27 | 15 |
| 1,2-Dichloroethane | 13,8 | 62 | 27 | 15 |
| 1,2-Dichloropropane | 15,2 | 78 | 41 | 15 |
| 1,2-Dichloropropane | 15,2 | 76 | 41 | 15 |
| 1,2-Dichloropropane | 15,2 | 63 | 27 | 15 |
| 1,3-Dichloropropene | 16,2 | 112 | 77 | 10 |
| 1,3-Dichloropropene | 16,2 | 75 | 49 | 20 |
| 1,3-Dichloropropene | 16,2 | 75 | 39 | 15 |
| 1,2-Dibromoethane | 18,4 | 109 | 27 | 20 |
| 1,2-Dibromoethane | 18,4 | 107 | 107 | 5 |
| 1,2-Dibromoethane | 18,4 | 107 | 27 | 20 |

## 3. RESULTS

The method was tested on 3 representative matrices (pistachio, rice and a mix of cereals and dried pulses) verifying precision, sensitivity, linearity and matrix effect, and recovery.

### Precision

Precision was tested by repeatability tests at the concentration level of 10µg/kg (pistachio & cereals) and 20µg/kg (rice).

Repeatability at low concentrations *Tabella 2*

| Analyte | Pistachio 10µg/kg | Rice 20µg/kg | Cereals & Pulses mix 10µg/kg |
|---|---|---|---|
| 1,2-Dicloropropane | 2,6% | 8,6% | 1,7% |
| 1,3-Dicloropropene | 2,9% | 6,9% | 6,0% |
| Carbon tetrachloride | 4,7% | 6,5% | 1,8% |
| 1,2-Dibromoetane | 4,2% | 6,8% | 8,2% |
| 1,2-Dichloroetane | 4,0% | 5,5% | 4,8% |

### Sensitivity

LODs (limits of detection) were estimated via calibration approach, according to Equation C, JRC Technical Reports: "Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food".
LOQs (limits of quantification) were estimated as 3.3 times LODs.

Limits of detection and quantification (LODs & LOQs) *Tabella 3*

| Analyte | Pistachio | | Rice | | Cereals & Pulses mix | |
|---|---|---|---|---|---|---|
| | LOD | LOQ | LOD | LOQ | LOD | LOQ |
| 1,2-Dicloropropane | 2,8 | 9,2 | 0,5 | 1,7 | 1,5 | 5,0 |
| 1,3-Dicloropropene | 2,7 | 8,9 | 2,1 | 6,9 | 2,7 | 8,9 |
| Carbon tetrachloride | 1,7 | 5,6 | 1,0 | 3,3 | 1,7 | 5,6 |
| 1,2-Dibromoetane | 2,0 | 6,6 | 0,8 | 2,6 | 1,3 | 4,3 |
| 1,2-Dichloroetane | 2,2 | 7,3 | 1,7 | 5,6 | 1,8 | 5,9 |

### Linearity & matrix effect

Linearity was tested in the range 10-200 µg/kg
The response is linear in the chosen range, but a noticeable matrix effect is noted.
In particular, in the rice matrix, the response seems significantly lower than in the other 2 matrices.
The pistachio matrix and cereals and pulses mix matrix respond in a similar way and within the tolerances set by the guidelines.

### Chromatograms and calibration curves

*Figura 2A*

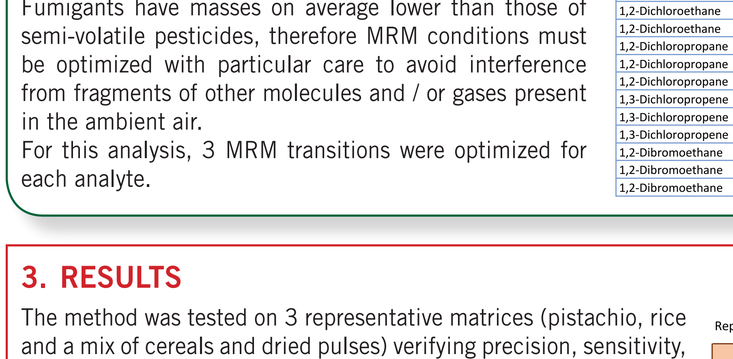






*Figura 2*

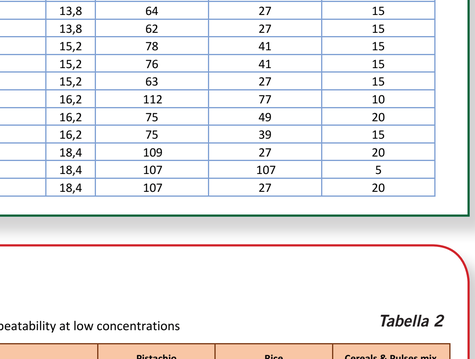



*Figura 3A*

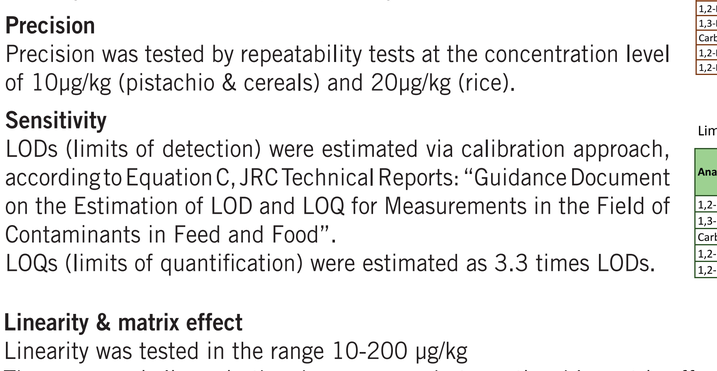






*Figura 3*

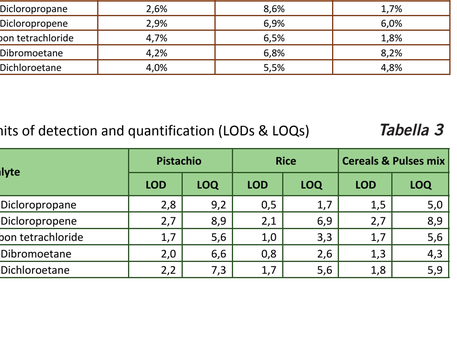
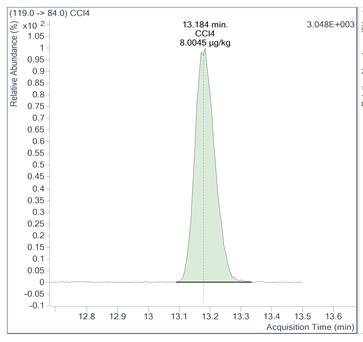



*Figura 4A*



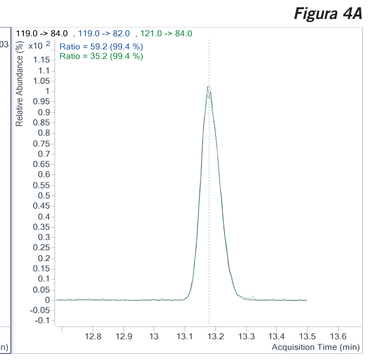




*Figura 4*

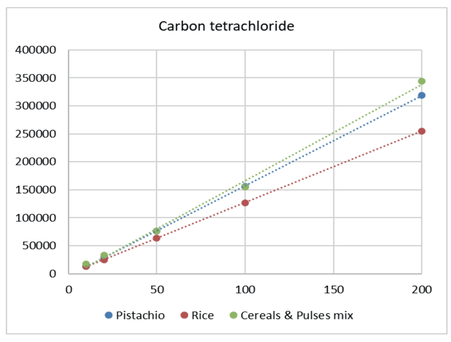
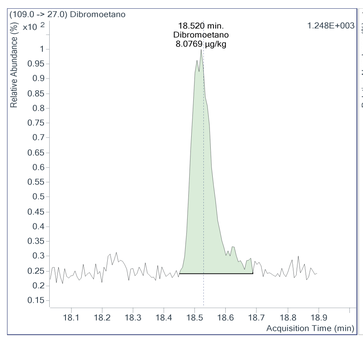



*Figura 5A*



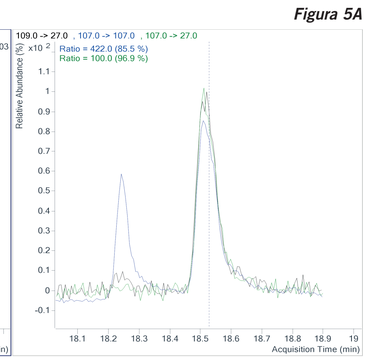




*Figura 5*

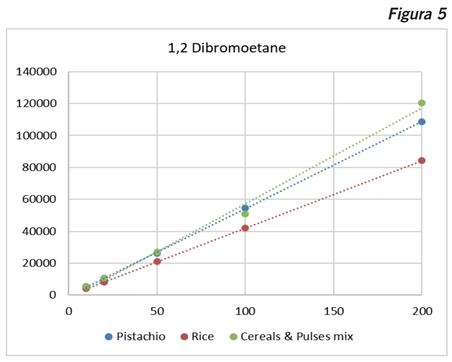
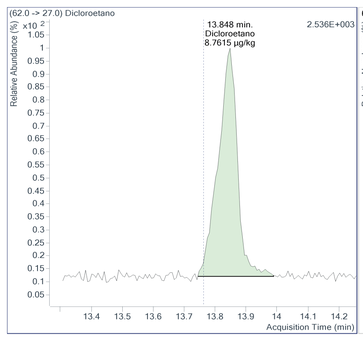



*Figura 6A*



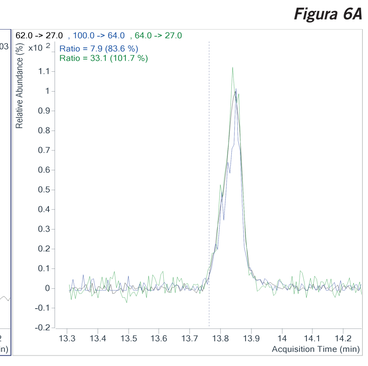
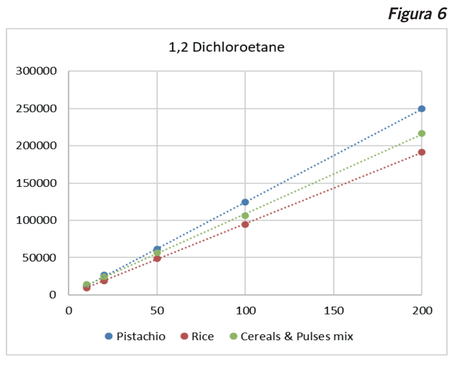




*Figura 6*




### Recoveries

Recovery was tested at the concentration level of 10µg/kg (pistachio & cereals) and 20µg/kg (rice).

Recoveries *Tabella 4*

| Analyte | Pistachio 10µg/kg | Rice 20µg/kg | Cereals & Pulses mix 10µg/kg |
|---|---|---|---|
| 1,2-Dicloropropane | 100% | 93% | 82% |
| 1,3-Dicloropropene | 103% | 94% | 89% |
| Carbon tetrachloride | 94% | 97% | 82% |
| 1,2-Dibromoetane | 99% | 89% | 84% |
| 1,2-Dichloroetane | 106% | 88% | 90% |

## 4. CONCLUSIONS

This work shows that, by using optimized extraction and dedicated chromatographic conditions, the Quechers method can be used for the analysis of residues of very volatile substances such as fumigants.
The technical and performance requirements set out in the SANTE/12682/2019 guidelines are met.

SANTE/12682/2019: Validation parameters and criteria *Tabella 5*

| Parameter | Criterion | Tested | Met |
|---|---|---|---|
| Sensitivity/linearity | Deviation of back calculated concentration from true concentration 20 % | Yes | Yes |
| Matrix effect | | Yes | Yes, There are matrix effects that can be compensated by matrix matched calibration or standard addition or using isotopically labelled internal standard |
| LOQ | ≤MRL | Yes | Yes |
| Specificity | Respons of reagent blank ≤ 30% RL | Yes | Yes |
| Recovery | 70-120% | Yes | Yes |
| Precision (RSDr) | ≤20% | Yes | Yes |
| Precision (RSDwr) | ≤20% | No | |
| Robustness | Average recovery and RSD wR, derived from on going method validation/verification | No | |
| Ion ratio | | Yes | Yes |
| Retention time | ± 0,1min | Yes | Yes |

The matrix effects found are not different from those that can be encountered with the analysis of other pesticides by applying this method, they are known and very well controlled through the application of some techniques such as: the use of isotopically labelled internal standards, or by means of matrix-matched calibration or by applying the standard addition technique.
Other volatile compounds, fumigants and metabolites with the same properties can be analyzed in the same way after careful optimization of the instrumental conditions.

**CONTATTI**

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