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Development of A New Essay Method of Pesticides in Strawberries by GC-MS and Determination of their Residues in A Few Samples.

Khalid Laarej^a, Mohammed Jbilou^a, Rachid Alami^a

^a Department of Toxicology-Pharmacology, Laboratory of Research and Medical Analyzes (LRAM), The Fraternal of the Royal Gendarmerie 10100 Rabat, Morocco.

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ABSTRACT

Strawberries, fruits of the family Rosaceae (*Fragaria vulgaris* L), grown in Morocco in the regions of Souss, Gharb and Loukkos, are widely consumed because of their high vitamin content (C, B1, P and PP) and in mineral salts. This crop is very sensitive to parasites which require treatments with pesticides to preserve the crop. Our job is to develop a new analytical method based on the extraction of pesticide residues from strawberries samples and their GC-MS assay. The sample preparation consists of crushing the fruit and weighing 10 g for extraction by the QuEChERS method and 3 µl of the extract are injected into the GC-MS. The recovery percentage of this method is 87.5%, the detection limits are 10 PPB and the linearity repetition coefficient is greater than 0.99. 17 samples taken on the market were analyzed by this method, the results showed that a sample is positive in Mepanipyrim.

1. Introduction

The strawberry (*Fragaria vulgaris* L) [1], is a perennial plant native to America and belonging to the Rosaceae botanical family. It is of a high nutritional quality; rich in vitamins (C, B1, P and PP) and in mineral salts [2]. The main regions producing strawberries in Morocco are Souss, Gharb and Loukkos.

Strawberries are fruits and vegetables that are grown for a very short time of the year and consumed very quickly just after harvest and often without prior washing. The mode of their production above ground promotes the development of molds, hence the massive use of fungicides, but also insecticides especially for crops in economically viable conditions [3], which can lead to some risk for the presence of residues of these pesticides at the time of harvesting the fruit if the pre-harvest deadlines (DAR) corresponding to the pesticides used are not respected [4]. Apart from pesticides that are authorized by the National Office of Food Safety (ONSSA) for the cultivation of strawberry some farmers use other more toxic molecules [5] and therefore can significantly affect human health [6]. Our goal is to identify and measure pesticide residues by GC-MS in locally marketed strawberry samples and

compare their results with the European Committee's Maximum Residue Limits (MRL) [7], to inform consumers about the dangers of this uncontrolled production and marketing of strawberries in local markets.

2. Materials and Methods

Instrumentation

The gas chromatographic system coupled to the mass spectrometry used in this work is GC-MS Clarus with an automatic injector. The system is driven by software Turbo Mass Software (Microsoft Windows XP SP2). The stationary phase is a supelco® column (L 30mx ID 0.25X DF0.25) phase Elite-5MS.

Reagents and chemicals

Pesticide standards used in calibration range are LGC Standards

- Acetonitrile, Toluene and acetic acid VWR brand.
- SPEXQuE QuEChERS Kits (Citrate Buffer Extraction Tubes).
- ULTRA QUECH (QUEC-208).

Calibration range

*Corresponding author.

The preparation of the calibration range (0.01 ppm, 0.02ppm, 0.03 ppm, 0.1 ppm and 0.2 ppm) was made from the stock solution of a mixture of 1ppm of 39 pesticides on a sample of organic strawberry, brought back of a vegetable and organic fruit trader in Rabat.

(Difluorobenzamide, Aminocarb, Chlomephos, Methiocarb, Ethoprophos, Chlorbufam, Monolinuron, Sebumeton, Iprobenfos, Pirimicarb, Benonacor, Chlorpyriphosdesmethyl, Toclophosmethyl, Malathion, Fenpropidin, Fenpropimorph, Parathion, Triadimephon, Pirmphosethyl, Cyprodinil, Penconazol, Parathion, Zoxamide, Procmidon, Methidathion, Mepanipyrim, Flutiafol, Oxadiazon, Binapacryl, Ofurace, Trifloxystrobin, Spiromesifen, Fenpropathrin, Pyriproxyfen, L-cyathothrin, Fenarimol, Deltamethrin, Indoxacarb and Pyridaben) at 1ppm by successive dilutions. Sulfotep was used as an internal standard and triphenylphosphate (TPP) as an external standard at 0.1 ppm each.

Collection and origin of strawberry samples

The strawberry samples were randomly selected from sales points in Rabat, Salé, Kenitra and Meknes. These samples were selected and coded according to their origins (Table 1).

Extraction by the method of QuEChERS

Extraction: Transfer 5-10 g of the homogenate from the strawberry sample in to a 50 mL conical tube, add 10mL of the acetonitrile solution to 1% acetic acid, 100µL of the internal standard and mix. with the SPEXQuE Acetate Tube container (AOAC-ACE-50 mL). Vortex for 1 min and centrifuge at 3000 rpm for 5 min.

Purification: Transfer 1 mL to SPEXQuE PSA 2 mL tube (ULTRAQuECh-QUEC-208). Vortex for 1min and centrifuge at 3000 rpm for 5 min. Fill a glass tube with 0.5 mL of the extract and evaporate to dryness under a stream of nitrogen. Resume the dry extract with 50 µl of toluene and vortex for 1 min. Transfer the extract into the injection vial and inject 3µl into GC-MS in splitless mode.

Chromatographic conditions

The oven was programmed from 90°C up to 230°C at a gradient of 15 °C per min and then at 5 °C per min up to 290 ° C with pre-heating of the transfer line to 300 °C and the ionization source at 250°C. The automatic injection is in splitless mode (50/1 to 250 °C). Ionization is caused by an electronic impact (IE) and the carrier gas is helium at the rate of 0.8ml/min

3. Results and discussion

Chromatogram of the standard

After analysis, the chromatogram showing the peaks of the pesticides that make up the mixture was recorded in Figure 1, the detection limits (LD) are at 10 PPB and the numerical results; Standard concentration (Cc), Retention time (RT), detection and quantification (m/z) masses, Found

concentration(Ct), and average parentage of extraction yield were shown in Table 2.

Linearity

Over a concentration range consisting of 5 levels of concentrations (0.01ppm, 0.02ppm, 0.03ppm, 0.1ppm and 0.2 ppm), we studied the equation of the calibration line ($Y= ax+b$) of each pesticide and we computed by the least squares method over the entire range the satisfactory R^2 repetition coefficients (Figure 2 and Table 3).

Determination of pesticide residues in strawberry samples

The application of the pesticide assay method by GC-MS on locally marketed strawberry samples showed the presence of Mepanipyrim residues at 0.016 mg / kg in EFR3 (MRL EUR 0.01 mg / kg) [7] and L-cyathothrin at 0.033 mg /kg in EFR5 (MRL EUR 0.20mg / kg) [5] (Figure 3 and Table3). The exceedances of the tolerated limits come mainly from the bad methods of treatment of strawberry crops by certain farmers who do not respect the deadlines before harvests (DAR) recommended by the manufacturer [8]. Mepanipyrim is a toxic fungicide, acts effectively on gray mold (*Botrytis cinerea*) [9], however the persistence of these residues on fruit crops (strawberry) directly to local consumers can affect their health and generate cases of pathological diseases cancer [10]. L-cyathothrin is an insecticide that acts on the nervous system and the persistence of these residues in strawberries can lead to cases of human neurotoxicity [11] and could affect the development of the child's nervous system [12] (Table 4).

3.1. Tables & Figures

3.2. 1. Tables

Table1: Origins of strawberry samples.

Strawberries codes	Dates	Quantities	Nature
EFR1	06.02.2019	250 g	Ripe strawberries
EFR2	13.02.2019	250 g	Ripe strawberries
EFR3	20.02.2019	250 g	Ripe strawberries
EFR4	10.02.2019	125 g	Ripe strawberries
EFR5	13.02.2019	125 g	Ripe strawberries
EFS6	20.02.2019	125 g	Ripe strawberries
EFS7	22.02.2019	125 g	Ripe strawberries
EFS8	10.02.2019	125 g	Ripe strawberries
EFS9	01.03.2019	125 g	Ripe strawberries
EFK10	05.03.2019	125 g	Ripe strawberries
EFK11	09.02.2019	250 g	Ripe strawberries
EFK12	15.02.2019	250 g	Ripe strawberries
EFK13	26.02.2019	250 g	Ripe strawberries
EFM14	28.02.2019	250 g	Ripe strawberries
EFM 15	30.03.2019	250 g	Ripe strawberries
EFM 16	15.03.2019	250 g	Ripe strawberries
EFM 17	15.03.2019	250 g	Ripe strawberries

Table 2: Analytical parameters of mixture pesticides.

Pesticides	Cc(ppm)	TR (min)	Masses pics (m/z)	Pics Qt (m/z)	Ct(ppm)
Difluorobenzamide	0.1	06.06	141.113.63	141	0.07
Aminocarb	0.1	06.29	151.150.136	151	0.07
Monolinuron	0.1	09.48	61.46.126	61	0.08
Pirimicarb	0.1	10.12	72.166.42	72	0.09
Toclophosméthyl	0.1	10.47	265.125.93	265	0.06
Malathion	0.1	10.61	93.173.125	93	0.09
Fenpropidin	0.1	11.04	97109.139	97	0.08
Fenpropimorph	0.1	11.13	128.129.117	128	0.08
Pirimphosethyle	0.1	11.47	168.152.180	168	0.09
Cyprodinil	0.1	11.63	224.225.77	224	0.08
Penconazol	0.1	11.82	159.248.161	159	0.07
Parathion	0.1	11.99	109.97.125	109	0.07
Zoxamide	0.1	12.04	187.242.189	187	0.10
Procymidon	0.1	12.09	96.67.53	96	0.08
Méthidathion	0.1	12.27	85.145.93	85	0.06
Mepanipirim	0.1	12.46	222.223.77	222	0.07
Flutriafol	0.1	12.62	123.164.95	123	0.08
Oxadiazon	0.1	12.93	41.43.175	41	0.10
Clodinafop	0.1	13.04	238.266.130	238	0.08
Binapacryl	0.1	13.36	83.55.84	83	0.10
Trifloxystrobin	0.1	14.55	116.131.59	116	0.08
Spiromesifen	0.1	15.68	57.99.71	57	0.09
Fenpropathrin	0.1	16.15	97.55.43	97	0.10
Pyriproxyfen	0.1	17.06	136.78.96	136	0.06
L-cyalthrine	0.1	17.10	181.197.208	181	0.07
Pyridaben	0.1	18.87	147.117.132	147	0.07
Indoxacarb	0.1	23.02	59.203.150	59	0.06
Deltamethrine	0.1	23.11	181.77.253	181	0.07
Average parenting performance					87.50%

Table 3: Results of linearity.

Pesticides	Y=(ax+b)	R2
Difluorobenzamide	0.0103x+0.0065	0.997
Aminocarb	0.0097x+0.0104	0.995
Monolinuron	0.0115x+0.0144	0.999
Pirimicarb	0.0093x+0.0065	0.998
Toclophosméthyl	0.0083x+0.0065	0.998
Malathion	0.0153x+0.0065	0.999
Fenpropidin	0.0118x+0.0065	0.998
Fenpropimorph	0.0093x+0.0065	0.996
Pirimphosethyle	0.0115x+0.0065	0.998
Cyprodinil	0.0033x+0.0065	0.998
Penconazol	0.0190x+0.0065	0.991
Parathion	0.0188x+0.0065	0.998
Zoxamide	0.0119x+0.0065	0.995
Procymidon	0.0183x+0.0065	0.994
Méthidathion	0.0098x+0.0065	0.994
Mepanipirim	0.0140x+0.0065	0.999
Flutriafol	0.0091x+0.0065	0.997
Oxadiazon	0.0100x+0.0065	0.998
Clodinafop	0.0106x+0.0065	0.995
Binapacryl	0.0130x+0.0065	0.997
Trifloxystrobin	0.0105x+0.0065	0.997
Spiromesifen	0.0095x+0.0065	0.995
Fenpropathrin	0.0111x+0.0065	0.999
Pyriproxyfen	0.0133x+0.0065	0.998
L-cyalthrine	0.0114x+0.0065	0.999
Pyridaben	0.0166x+0.0065	0.998
Indoxacarb	0.0139x+0.0065	0.993
Deltamethrine	0.0167+0.0065	0.995

Table 4: Dosage Results of Pesticide Residues in Strawberry Samples by GC-MS.

Strawberries codes	Search	Dosage	MRL EU	DAR	Interpretations
EFR1	< LD	-	-	-	-
EFR2	< LD	-	-	-	-
EFR3	Mepanipirim	0.016 mg/kg	0.010 mg/kg	3 days	> LMR UE
EFR4	< LD	-	-	-	-
EFR	L-cyathothrine	0.033 mg/kg	0.200 mg/kg	7 days	< LMR UE
EFS6	< LD	-	-	-	-
EFS7	< LD	-	-	-	-
EFS8	< LD	-	-	-	-
EFS9	< LD	-	-	-	-
EFK10	< LD	-	-	-	-
EFK11	< LD	-	-	-	-
EFK12	< LD	-	-	-	-
EFK13	< LD	-	-	-	-
EFM14	< LD	-	-	-	-
EFM15	< LD	-	-	-	-
EFM16	< LD	-	-	-	-
EFM17	< LD	-	-	-	-

3.3. 2. Figures

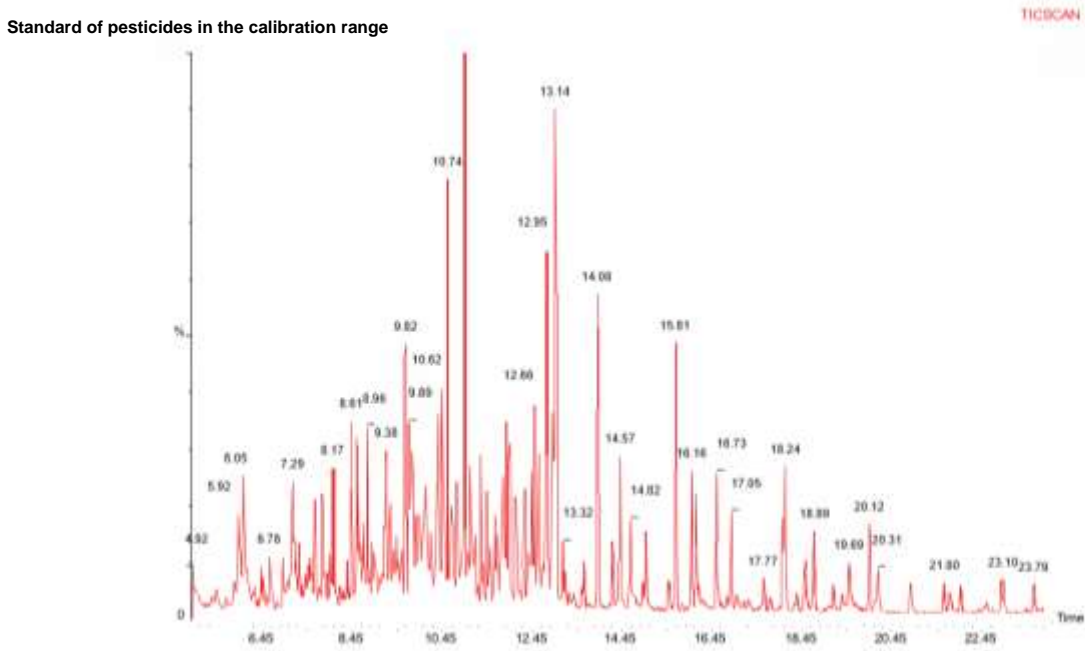


Fig 1: Chromatogram of the standard

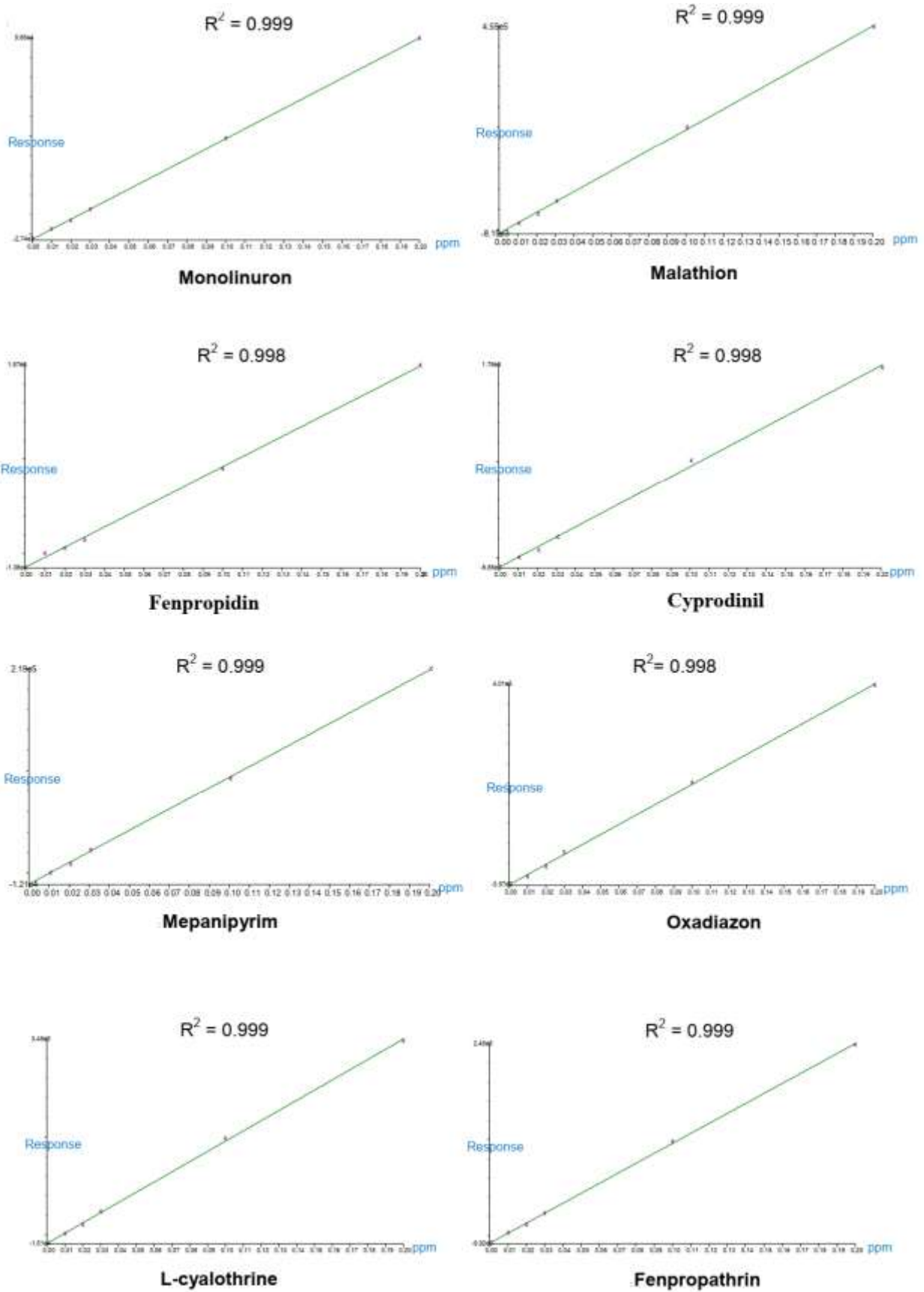


Fig 2: Examples of calibration lines for mixed pesticides

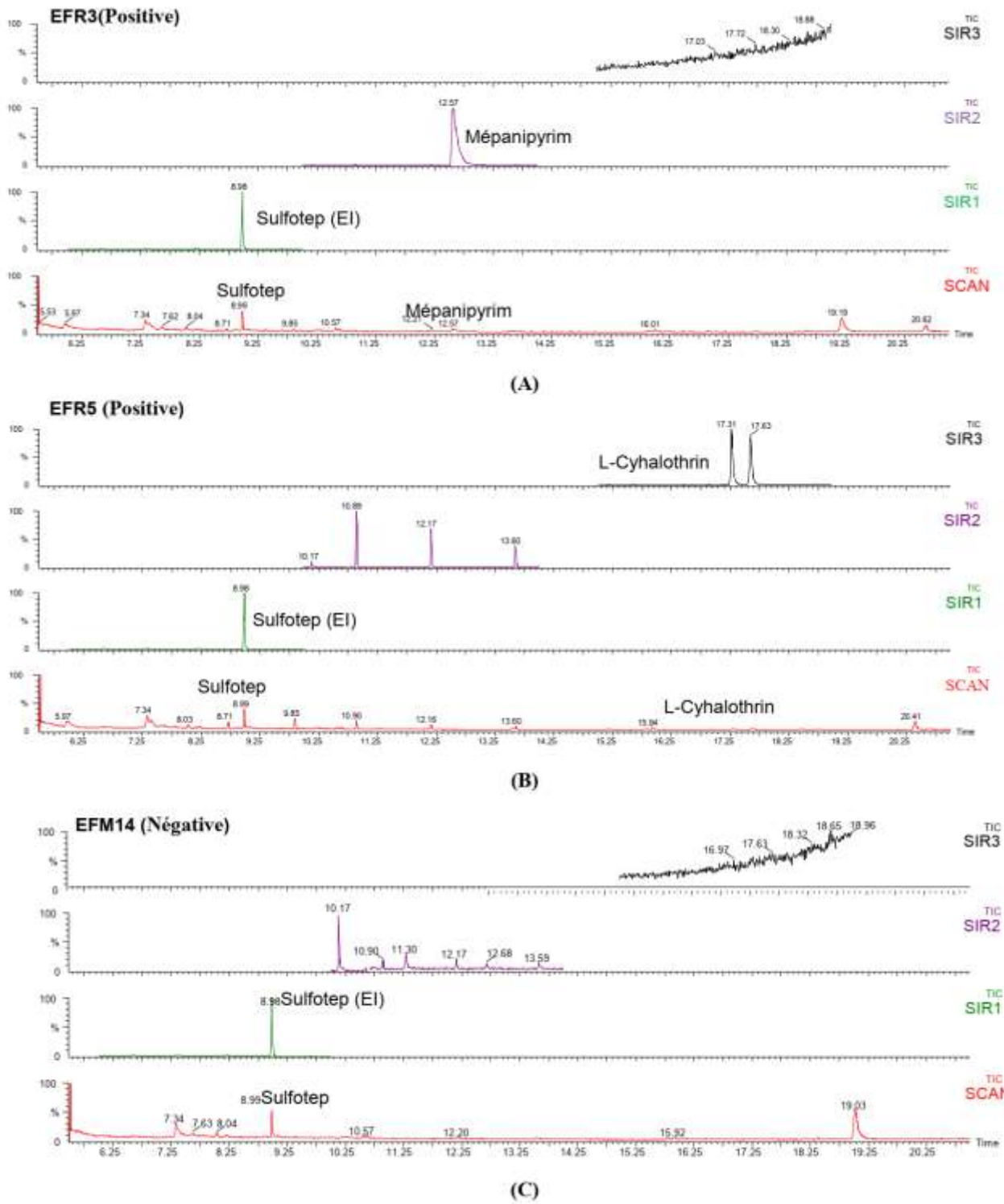


Fig 3 : Chromatograms of the samples (A, EFR3, B, EFR5 and C, EFM14)

4. Conclusion

The determination of pesticide residues by GC-MS in locally marketed strawberry samples has shown that these fruits are contaminated with pesticide residues; L-cyhalothrin at a concentration lower than European standards and Mepanepirim at a concentration above European standards. This study is only preliminary and should be extended to other regions of Morocco to take the necessary measures to preserve health consumers.

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