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**Feasibility of LC/TOFMS and Elemental Database Searching
As a Spectral Library for Pesticides in Food**

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Feasibility of LC/TOFMS and Elemental Database Searching As a Spectral Library for Pesticides in Food

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Abstract

Traditionally, the screening of unknown pesticides in food has been accomplished by GC/MS methods using conventional library searching routines. However, many of the new polar and thermally labile pesticides are more readily and easily analysed by LC/MS methods and no searchable libraries currently exist (with the exception of some user libraries, which are limited). Therefore, there is a need for LC/MS libraries that can detect pesticides and their degradation products. This paper reports an identification scheme using a combination of LC/MS time-of-flight (accurate mass) and an Access database of 350 pesticides that are amenable to positive ion electrospray. The approach is different from conventional library searching of fragment ions. The concept here consists of three parts. Firstly, initial screening of possible pesticides in actual market-place fruit extracts (apple and orange) using accurate mass and generating an accurate mass via an automatic ion extraction routine. Secondly, searching the Access database manually for a screening

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3 identification of a pesticide. Thirdly, identification of the suspected compound by
4 accurate mass of at least one fragment ion and comparison of retention time with an
5 actual standard. Imazalil and iprodione were identified in apple and thiabendazole in
6 oranges using this database approach.
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15 **Keywords:-** pesticide residues, LC/MS, TOF-MS, database, imazalil, iprodione,
16 thiabendazole
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22 **Introduction**

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24 The identification and quantitation of unknown pesticides in fruit and vegetables are
25 greatly important to individuals and health organizations around the world. In order
26 to meet these health concerns, the European Union (EU) and the US have set new
27 Directives for pesticides at low levels in vegetables. For example, new laws, such as
28 the European Directive 91/414/EEC or the Food Quality Protection Act (FQPA) in the
29 US, have changed the standards for human health, workers, and environmental
30 protection, which require lower levels of pesticides in food [EU Food Directives,
31 Food Quality Protection Act]. They also require re-registration for older pesticides.
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46 Furthermore, the review programs have withdrawn authorizations for many of the
47 crop protection products currently on the market, 177 compounds in US and 320 in
48 Europe. Moreover, it was announced in Europe that a total of 110 products would be
49 withdrawn in the near future (EU Directive 91/414/EEC). Furthermore, the revision
50 of the review program in Europe dictates that over 450 existing active substances will
51 be taken off the market by 2008 with about 400 pesticides remaining in use.
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Next, the quality standards within the new regulations include the re-assessment of the maximum residue limits (MRLs) for vegetables. EU directives are setting different MRLs for each pesticide within each food group, and typically, the MRLs are lower than the previous ones. Furthermore, the new directives also lead to different MRLs for each EU country, which are still being decided. EU directives state that the individual country MRLs will be maintained in the new program. Finally, banned compounds have the lowest MRLs, which is set now at 0.01 mg/kg (ppm). With the planned program to remove so many compounds from the market, it is important, even necessary, that screening for unknown pesticides may be done by LC/MS on vegetable extracts. Because it is not always possible to know which banned substances may be used, it is of vital importance to environmental food monitoring that there be a system of unknown identification to give fast and accurate screening of unknown substances in food and food products.

Thus, there is an important need for research studies and methods development on the analysis and screening of pesticides in food by new LC/MS methods, such as accurate mass screening using LC/TOFMS and database analysis [Ferrer and Thurman, 2003a; Thurman et al. 2005a, Thurman et al. 2005b; Garcia-Reyes et al. 2005]. This combined with the use of large accurate mass databases of pesticides is an important and useful new screening procedure, especially when accurate mass is less than 3-ppm accuracy.

The combination of LC/MS TOF and database screening consists of three steps, which are outlined in detail below. They are:

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1. Analyse the fruit or vegetable extract with LC/TOFMS in full scan looking for important unknown peaks using a mild in-source CID fragmentation.
2. Search the Access pesticide database using the accurate mass found in full scan for initial screening.
3. If samples screen positive for a pesticide, make identification using at least one fragment ion with its accurate mass combined with retention time.

This paper gives several detailed examples of this process using retail samples of apples and oranges, which show the screening by accurate mass and database entry, followed by identification of several pesticides that are major components of the samples.

Materials and Methods

Whole-vegetable extraction. Portions of apples (2 kg) were obtained from the market place and homogenized by chopping. Then 15 g portions of the homogenized chopped fruit were weighted into a 200 mL PTFE centrifuge tube. 45 mL ethyl acetate and 1 mL NaOH (6.5 M) were added and blended in a Polytron (high-speed blender) for 30 seconds at 21,000 rpm. The combined extracts were then filtered through a thin layer of 20 g of anhydrous Na₂SO₄. The solid was washed with 50 mL of ethyl acetate and the combined extracts were evaporated to dryness on a vacuum rotary evaporator using a water bath at 45 ± 5°C. The dried residue was dissolved by sonication in 15 mL of methanol. The extracts, which contained 1 g of sample per mL, were filtered through 0.2 µm PTFE filters (Millex FG, Millipore) prior to LC/TOFMS analysis.

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LC/TOFMS Methods. LC Pumps were HP 1100, injection volume 50 μ L, column: ZORBAX Eclipse® XDB 4.6x150 mm C-8, 5-micron, mobile phase A=ACN and B=0.1% formic acid in water, gradient was 15%A to 100%A over 30 minutes at a flow rate of 0.6 mL/min, model LC/MSD TOF (Agilent Corp, Santa Clara, CA, USA) with electrospray source positive ESI+, capillary 4000V, nebulizer 40 psig, drying gas 9 L/min, gas temp 300°C, fragmentor 190V, skimmer 60V, Oct DC1 37.5 V, OCT RF V 250V, reference masses (Agilent Solution): 121.0509 (purine) and 922.0098 (hexakis(1H, 1H, 3H-tetrafluoropropoxy)phosphazine) m/z, resolution: 9500 \pm 500 @ 922.0098 m/z, reference A sprayer 2 is constant flow rate (600 μ L/hr) during the run.

Results and Discussion

Creation of Access Database. Table 1 shows the list of 350 compounds that were used in the database for the search of pesticides in fruit extracts. The list consists of the three major classes of pesticides that are commonly used in Europe for treating crops of fruits and vegetables, as well as many of the pesticide degradation products. There are insecticides, herbicides, and fungicides. An Excel spreadsheet was used to calculate the accurate masses of each of the 350 pesticides. The compounds in the database are known to ionise in positive ion electrospray and were collated from a series of publications, as well as from approximately 100 standards analysed in our laboratory. Figure 1 shows the appearance of the Access database, called Pesticidas. The front page of the database has 4 basic key functions. The first is called “Find Accurate Mass” and consists of the accurate masses of all 350 pesticides to the fourth decimal place. The program searches these and finds all compounds that have the correct mass to the second decimal place. This allows for compounds that have either similar or identical accurate masses. It turns out that although accurate mass is a very

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3 powerful technique, it is possible for pesticides to have the same empirical formula,
4 and thus the same accurate mass! In fact in this database of 350 compounds, 8
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8 compounds have the same formula. This includes several degradate products of the
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10 triazines. These compounds also require retention time and fragment ions for a final
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12 confirmation.

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17 The second key of the database is "Find Pesticide". This key will locate any
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19 compound in the database and display its formula, structure, and accurate mass to 4
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21 decimal points. The third key is "New Pesticide" key, which is used to add new
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23 compounds to the database. The fourth key is "Edit List", which allows one to change
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25 parameters of the compounds within the database. The edit key is disabled when the
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27 program is used in the laboratory in order to protect the safety of the program from
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29 error entries. The fifth and last key is the "Exit" key, which exits the database
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31 program. The logo of the University of Almeria (Almeria, Spain) is also shown on
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33 the front page of the database.
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41 Advantages of using Access for this pesticide database is that this program is
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43 available as part of the software of Office (Microsoft) and thus is available to use on
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45 any computers that run XP Windows. The database is approximately 18 megabytes in
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47 size; thus, it is easily transported and available for use by other scientists that are
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49 working on pesticide analysis. It can be readily sent by email or by transfer by
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51 memory stick, CD etc. The database is used in manual mode by entering the accurate
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53 mass, this is a limitation at this time, which will be explained in the next section.
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4 *Database Search of Apple Extract.* Figure 2 shows the total ion chromatogram (TIC)
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6 for the extraction of a store purchased apple. There are approximately 20 major peaks
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8 in the chromatogram at retention times from 2 to 30 min. However, the matrix is not
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10 simple and over 1000 peaks are present in sample with a signal to noise of 10:1.
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12 However, in this manual application we are screening only the major peaks. Thus,
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14 two major peaks at 18.0 and at 25.3 min were screened as possible pesticides by the
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16 manual database search. Figure 2 shows an example positive pesticide screen. We
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18 start with an accurate mass, in this case, the m/z 297.0574 ion at 18.0 min. This ion
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20 was chosen because it is the protonated molecule of the peak at 18.0 min. The
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22 database gave a positive screen for imazalil (Figure 1). Here we differentiate between
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24 a screen and an identification of a pesticide.
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32 Screening is a test that shows that a possible pesticide is present based on an analysis
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34 that is inadequate for confirmation, but that is rapid and inexpensive (i.e. the database
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36 search of the molecular ion with a retention time). The identification is based on
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38 further analysis, which includes the accurate mass of the protonated molecule and a
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40 one fragment ion with the correct retention-time match.
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46 Thus, continuing with the example of a positive screen, the database works by first
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48 entering the accurate mass of the protonated molecule. The mass is checked versus
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50 the database to two decimal places (note the value of 297.06 showing in Figure 1).
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52 Next the compound name is entered in the database and the structure, formula, and
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54 accurate mass appear for imazalil. The accuracy in this case was a difference of
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56 0.0018 u or ~6 ppm. The error in accuracy was caused by the very high concentration
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58 of imazalil in the sample, which saturated the detector. Typically, the extracted ion
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3 should be less than 10^6 counts (10^5 is ideal), rather than the 10^7 value, which is two
4 orders of magnitude above the ideal accurate mass window [Ferrer and Thurman,
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11 quicker way is to take the accurate mass on the tail of the peak, which lowers the
12 counts by an order of magnitude and gives an accurate mass of 297.0557, which is
13 within 0.1 mD of the correct value (see Figure 1)! Note the lower intensity at 3×10^5
14 counts. This procedure completes the screen for imazalil, but the compound is not yet
15 identified. Identification requires more information including fragment ion and
16 retention time matching, which will be addressed in the following section. The sample
17 can either be diluted and re-injected or, more simply, a smaller volume, such as 5 μL
18 rather than the initial 50 μL can be injected. The concentration of imazalil is
19 estimated at approximately 0.5 ppm in this apple extract.
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34 Another screening example showing the power of the accurate mass and the database
35 is the second positive screen at 25.3 min, which had an accurate mass of 330.0409.
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Using this approach it has been possible to measure the mass of an electron with
reproducible results [Ferrer and Thurman, 2005]. Thus, this sample gave two positive
screens for pesticides, imazalil and iprodione.

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3 The database also works well on compounds that are not chlorinated. For example,
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5 Figure 4 shows the TIC for an orange extract and the exact mass for a large peak at
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7 7.6 minutes with a m/z of 202.0437. Entering the accurate mass in the database gives
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9 the formula and structure for only one compound, thiabendazole. Note that the mass
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11 spectrum also shows a sulphur isotope at m/z 204.0407, which is consistent with the
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13 structure of thiabendazole. Approximately 75% of the compounds in the pesticide
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15 database of 350 compounds contain Cl, Br, or S. These A+2 isotopes are useful in
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17 both the screening and the identification of the compounds. But they are not
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19 necessary as the next section will show.
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27 *Identification of Pesticides.* After the initial screening of the pesticides in the apple or
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29 orange extract, the next step is to identify the compounds. The usual approach is to
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31 acquire the standard and to measure both retention time and at least one fragment ion
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33 for identification [Stolker et al., 2003]. The accurate mass fragment ions for imazalil,
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35 iprodione, and thiabendazole are shown in Figure 5, along with the structure of the
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37 proposed fragment ion. According to the identification point system [Stolker et al.,
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39 2003, Ferrer and Thurman, 2003b], the high resolution accurate mass of the
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41 protonated molecule and the fragment ion give a total of 4 IPs, which is used for
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43 identification along with the ion ratio. The IP system also requires a resolving power
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45 of 10,000 (defined as 10% valley), which is not possible with benchtop TOF
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47 instrumentation. Thus, unfortunately these data do not meet the IP standard. We
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49 consider this a shortcoming of the IP system, which was designed with GC/MS in
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51 mind rather than benchtop LC/TOFMS. The quality of the measurements meet the
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53 requirement of identification but not of the IP system.
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Nonetheless, further information is also obtained from the characteristic chlorine isotope cluster of both the protonated molecules and the fragment ions in these two cases. Note that the two chlorine isotope signature is obtained for the protonated molecule of imazalil m/z 297.0574 and 299.0038 (Figure 2) and for its fragment ion at m/z 255.0086 and 257.0045 in Figure 5.

Iprodione also showed a two chlorine isotopic signature at m/z 330.0409 and 332.0387 (Figure 4) for the protonated molecule and m/z 244.9881 and 246.9853 for the fragment ion (Figure 5). These chlorine signatures show the presence of two chlorine atoms in both molecules and give valuable identification information. Likewise, thiabendazole has an accurate mass fragment ion at m/z 175.0340, which also has the S isotope signature at A+2 mass units for further confidence in the identification.

Note that this two-step procedure requires first the screening of the pesticide followed by an identification step. The goal of our project, ultimately, is to include this information in the database, both fragment ion and retention time, and to automate the process. However, one must note that when this occurs the database becomes more of a user database because the retention time conditions may be variable from instrument to instrument. This problem of variability has been solved in GC/MS by the use of retention time locking and standardized electron impact spectra. Eventually this problem may be solved in LC/MS by similar approaches. Variation in fragmentation intensity is not critical with the use of accurate mass since the accurate mass of the fragment ion gives its molecular formula. Thus, at this time the database approach

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3 remains a screening tool, but powerful and fast because only the molecular formula is
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5 needed.
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10 **Conclusions**

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12 The use of accurate mass LC/TOFMS combined with database searching is a
13 powerful example of a new wave of technology for screening of pesticides in food.
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15 The use of classical fragmentation libraries (i.e. comparison of spectra containing
16 multiple ions) with LC/TOFMS is not needed, rather the use of molecular formula
17 (accurate mass of the protonated molecule) and the accurate mass of fragment ion,
18 when combined with retention time gives the identity of compounds without the
19 worry of the intensity of the fragment ions and how this may vary from instrument to
20 instrument and matrix to matrix. Thus, it is the view of the authors that LC/TOFMS
21 will become a more important tool in the screening and identification of pesticides in
22 the near future. However, there are problems to address before database screening is
23 routine. First is the automation of the database. Second is to address the issue of false
24 positives and false negatives. Of these, the false positives are easier to deal with
25 because they involve the identification process. The false negative is more serious,
26 since a pesticide is present in the food but is not detected. Also the topic of resolving
27 power and identification points needs to be re-addressed in our opinion. These topics
28 will be the subject of our future work on databases and LC/TOFMS.
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52
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3 Andalucía". The first author acknowledges a grant from the University of Almeria for
4 support of the database work.
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Table 1. Continued, “Pesticidas”

Pesticide	Formula	MH	Pesticide	Formula	MH
Methidathion	C9H11NO4PS3	302.9691	Fenbuconazole	C18H17ON4	337.1214
Clofentazine	C14H8Cl2N4	303.0199	Bifentanol	C20H23NO2	338.1863
Cyanothiophos	C15H14NO3PS	304.0556	Phenyl mercuric acetate	C8H9HgO2	339.0303
Fenarimphos	C13H22NO3PS	304.1131	Dimelfuron	C15H19ON4O3	339.1218
Fenproginomorph	C20H33NO	304.2635	Pyridaphenthion	C14H17N2O4PS	341.0719
Diazinon	C12H21NO3PS	305.1083	Bifenox	C14H8Cl2NO5	341.9931
Priniphos-methyl	C11H20NO3PS	306.1036	Propiconazole	C15H17O2N2O2	342.0771
BUFFROFEZIN	C16H23NO5S	306.1635	THIOURANATE-METHYL	C12H14N4O4S2	343.0529
oxamide	C15H15ON2O3	307.0844	Prothiophos	C11H15O2O2PS2	344.9701
Fenazquin	C20H22NO	307.1805	Azinphos-ethyl	C12H16NO3PS2	346.0443
Quinoxifen	C18H8O2FNO	308.0040	TRIFLUMIZOLE	C15H15OF3NO	346.0928
TEBUCONAZOLE	C16H22NO3O	308.1524	Isofenphos	C15H24N4O4PS	346.1236
DIFLUBENZURON	C14H20F2N2O2	309.0248	Tolyflusnid	C10H13O2FN2O2S2	346.9852
Isazofos	C9H17ON3O3PS	314.0490	Coroxon	C14H16CO6P	347.0446
Isaxathion	C13H16NO4PS	314.0610	Gibberelic acid	C19H34O6	349.1646
Triazophos	C13H16NO3PS	314.0723	Oclinalop-Propargyl	C17H13OF3NO4	350.0590
Hexaconazole	C14H17ON2O4	314.0821	Fenpropathrin	C22H33NO3	350.1751
Kresoxim-methyl	C18H19NO4	314.1387	Propargite	C19H26O4S	351.1625
Malaoxon	C10H19O7PS	315.0662	Hexythiazox	C17H21ON2O2S	353.1085
Nuarimol	C17H12O2FN2O	315.0695	TEBUFENQZIDE	C22H28NO2	353.2224
Flusilazole	C16H15F2N3S	316.1076	THIODICARB	C10H8N4O4S3	355.0563
Bupirimate	C13H24NO3S	317.1642	TRIFLUMURON	C15H10OF3N2O3	357.0259
Phosmet	C11H12NO4PS2	318.0018	G-LORSULFURON	C12H12ON2O4S	358.0372
Azinphos-methyl	C10H12NO3PS2	318.0130	Chlorfenvinphos	C12H14O3O4P	358.9788
Trilconazole	C17H20ON3O	318.1368	OXY FLURFEN	C15H11OF3NO4	360.0256
Melconazole	C17H22ON3O	320.1524	FLORA SULAM	C12H8F3N5O3S	360.0373
PROVALICARB	C18H28NO3	321.2173	CLETHODIM	C17H26ON3O3S	360.1395
Flamprop	C16H13OF3NO3	322.0641	Haloxypol	C15H11OF3NO4	362.0401
Pyriproxyfen	C20H19NO3	322.1438	Fenoxaprop-ethyl	C18H26ON3O5	362.0790
Sulfotep	C8H20O6P2S2	323.0300	Coumaphos	C14H16CO6PS	363.0217
Sulprofos	C12H19O2PS3	323.0358	Flufenacet	C14H18F4NO2S2	364.0737
EPN	C14H14NO4PS	324.0454	Benzoximate	C18H18ON3O5	364.0946
Azamehthiophos	C9H10ON2O3PS	324.9809	Flamprop-isopropyl	C19H19OF3NO3	364.1110
Diniconazole	C15H17O2N3O	326.0821	Tetrachlorvinphos	C10H8Cl4O4P	364.9065
Benalaxyl	C20H23NO3	326.1751	Pyridaben	C19H25ON2O5S	365.1449
ISOXAFLLITOLE	C12H15F3NO4S	327.0747	Dinocap	C18H24NO6	365.1707
Fluazifop acid	C15H12F3NO4	328.0791	Phosalone	C12H15ON4O4PS2	367.9941
Diclobutrazol	C15H19O2N3O	328.0978	Methoxyfenozide	C22H28NO3	369.2173
oxygen	C11H15O2NO3	328.9929	IOXYNIL	C7H8NO	369.8231
Pencycuron	C19H21ON2O	329.1415	AMIDOSULFURON	C9H15NO5S2	370.0486
brodione	C13H14O2N3O3	330.0407	Thiophanate ethyl	C14H18N4O4S2	371.0842
Mecarbam	C10H20NO5PS2	330.0593	TETRAOCONAZOLE	C13H11O2F4NO3O	372.0288
Epoxiconazole	C17H13OF3NO4	330.0804	Profenofos	C11H15F5O3PS	372.9424
Fluridone	C19H14F3NO	330.1100	QUICALFOF-ETHYL	C19H17ON2O4	373.0950
Diachtal	C10H8O4O4	330.9093	Pyrazophos	C14H20NO5PS	374.0934
Fenarimol	C17H12O2N2O	331.0399	Famoxadone	C22H28NO4	375.1339
Malathion	C10H19O6PS2	331.0433	Phosfon	C20H4Cl2O2P	375.1770
Dichlofluanid	C9H11O2FN2O2S2	332.9696	Bromuconazole	C13H13BrO2N3O	375.9614
Flurtamone	C18H14F3NO4	334.1049	Fluquinconazole	C16H8Cl2FNO5	376.0163
Priniphos-ethyl	C13H24NO3PS	334.1340	Pochlozox	C14H16F3NO3O2	376.0981
Tabufenpyrad	C18H15F3NO3	334.1637	FLAZASULFURON	C13H15F3NO5	376.0981
Flamprop-methyl	C17H15OF3NO3	336.0797	FLAZASULFURON	C13H15F3NO5	376.0983
Coquatocet-Mexyl	C18H22ON3O	336.1361	Clethodim sulfioxide	C17H26ON4O4S	376.1344

Pesticide	Formula	MH
Etofenprox	C25H28O3	377.2111
Naled	C4H7Br2C2O2P	378.7898
Endrin	C12H8Cl6O	378.8779
Dieldrin	C12H8Cl6O	378.8779
PYRIDATE	C19H23ON2O2S	379.1242
TEFLUBENZURON	C14H8O2F4N2O2	380.9815
Carbosulfan	C20H32N2O3S	381.2206
Metsulfuron	C14H15N2O6S	382.0816
FLURA THIOCARB	C18H26N2O5S	383.1635
Fluazifop-butyl	C19H20F3NO4	384.1417
Ethion	C9H22O4P2S4	384.9949
Thiencisulfuron methyl	C12H13N5O6S2	388.0380
DIMETHOMORPH	C21H22ON4O	388.1310
Clethodim sulfon	C17H26ON3O5S	392.1293
Dialfos	C14H17ON4O4PS2	394.0998
Diflufenican	C19H11F5N2O2	395.0813
Rotenone	C23H22O6	395.1489
Tribenuron methyl	C15H18N2O6S	396.0972
TRIASULFURON	C14H16ON2O5S	402.0633
AZOXYSTROBIN	C22H17N3O5	404.1241
Difenoconazole	C19H17O2N3O3	406.0720
Flazasulfuron	C13H12F3N5O5S	408.0584
Trifloxystrobin	C20H19F3N2O4	409.1370
Bensulfuron-methyl	C16H18N4O7S	411.0969
INCOSULFURON	C15H18N6O5S	411.1081
Bentfluracarb	C20H18ON2O5S	411.1948
CINOSULFURON	C15H19NO7O5S	414.1078
Metsulam	C14H13O2N5O4S	418.0138
HALOXYFOP-ETHOXYETHYLESTER	C19H19OF3NO4	418.1027
PROSULFURON	C15H16F3N5O4S	420.0948
Fenpyroximate	C24H27N3O4	422.2074
Rimsulfuron-methyl	C14H17ON2O7S2	432.0642
Haloxypol-etolyl	C19H19OF3NO5	434.0977
HEXAFUMURON	C16H8O2F6N2O3	458.9743
Sulfosulfuron	C19H21N5O7S2	468.0894
Primsulfuron-methyl	C15H12F4N4O7S	468.0436
FLUFENOXURON	C21H11OF6N2O3	489.0495
Trisulfuron methyl	C17H19F3N6O6S	493.1112
Deltamethrin	C22H19Br2NO3	503.9804
LUFENURON	C17H8O2F6N2O3	510.9857
INDOXYACARB	C22H17OF3N3O7	528.0780
Chlorfluzuron	C20H8Cl3F5N3O3	539.9702
Acrinathrin	C26H21F6NO5	542.1397
SPINOSYN D	C21H25NO10	732.4681
Avermectin B1b	C47H70O14	859.4844
Avermectin B1a	C48H72O14	873.5000

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The figure illustrates a database search process for accurate mass. It shows three main components:

- Principal : Form:** The main interface with buttons for "Find Formula", "Find Accurate Mass", "Find Pesticide", "Exit", "New Pesticide", and "Edit List". The "Find Accurate Mass" button is highlighted with a red circle.
- Enter Parameter Value:** A dialog box where the parameter "mass" is set to "297.0574".
- Find Pesticide:** A table showing search results for pesticides. The entry for "IMAZALIL" is highlighted with a red circle.
- IMAZALIL Detail:** A detailed view of the pesticide "IMAZALIL", showing its chemical structure, formula $C_{14}H_{14}Cl_2N_2O$, and the calculated mass $[M+H] 297.0556$.

Figure 1. Access database search for accurate mass of the m/z 297.0574 ion.

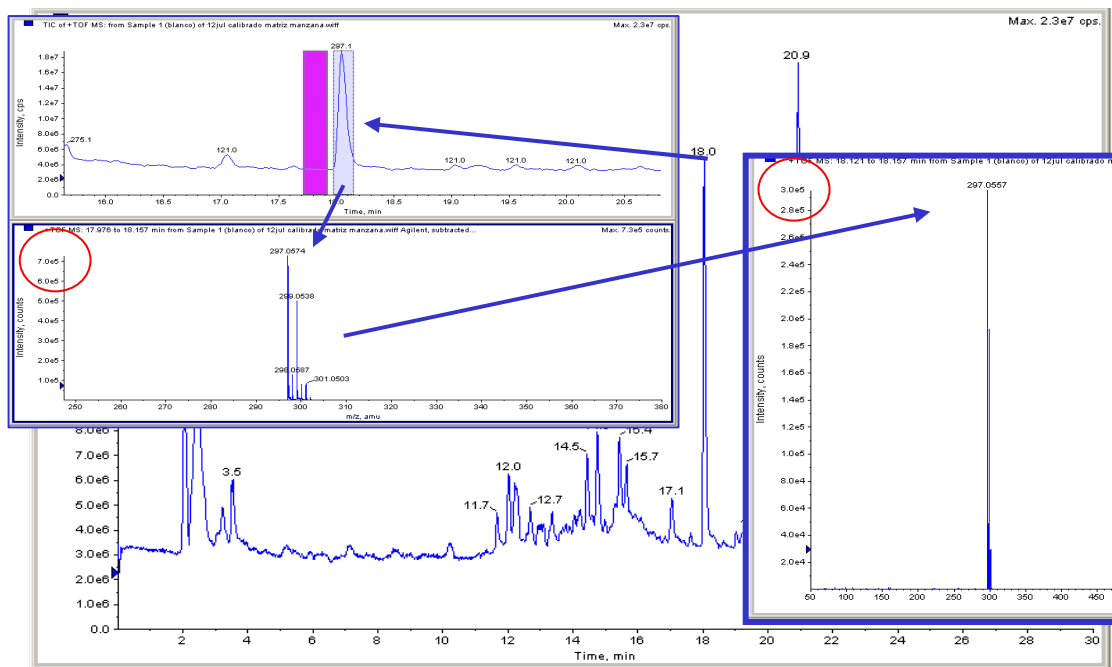


Figure 2. Total ion chromatogram of apple extract using LC/TOFMS.

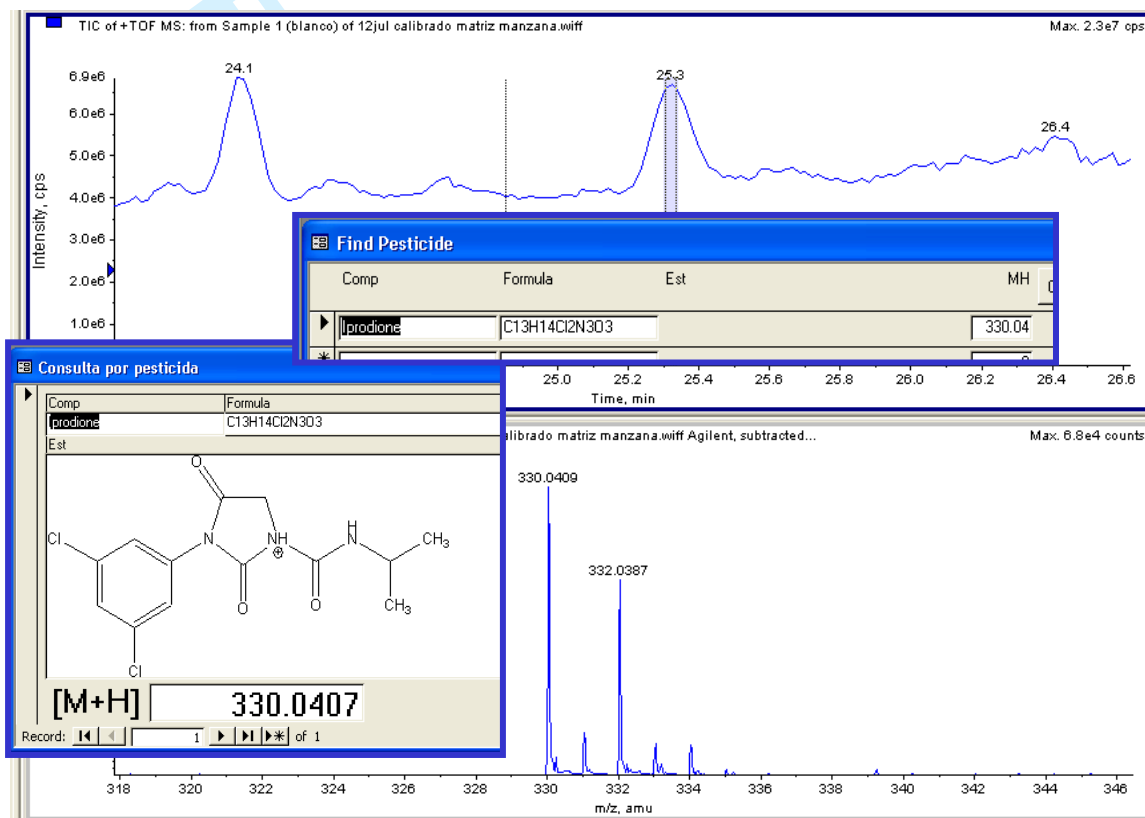


Figure 3. Accurate mass screening for mass of m/z 330.0409.

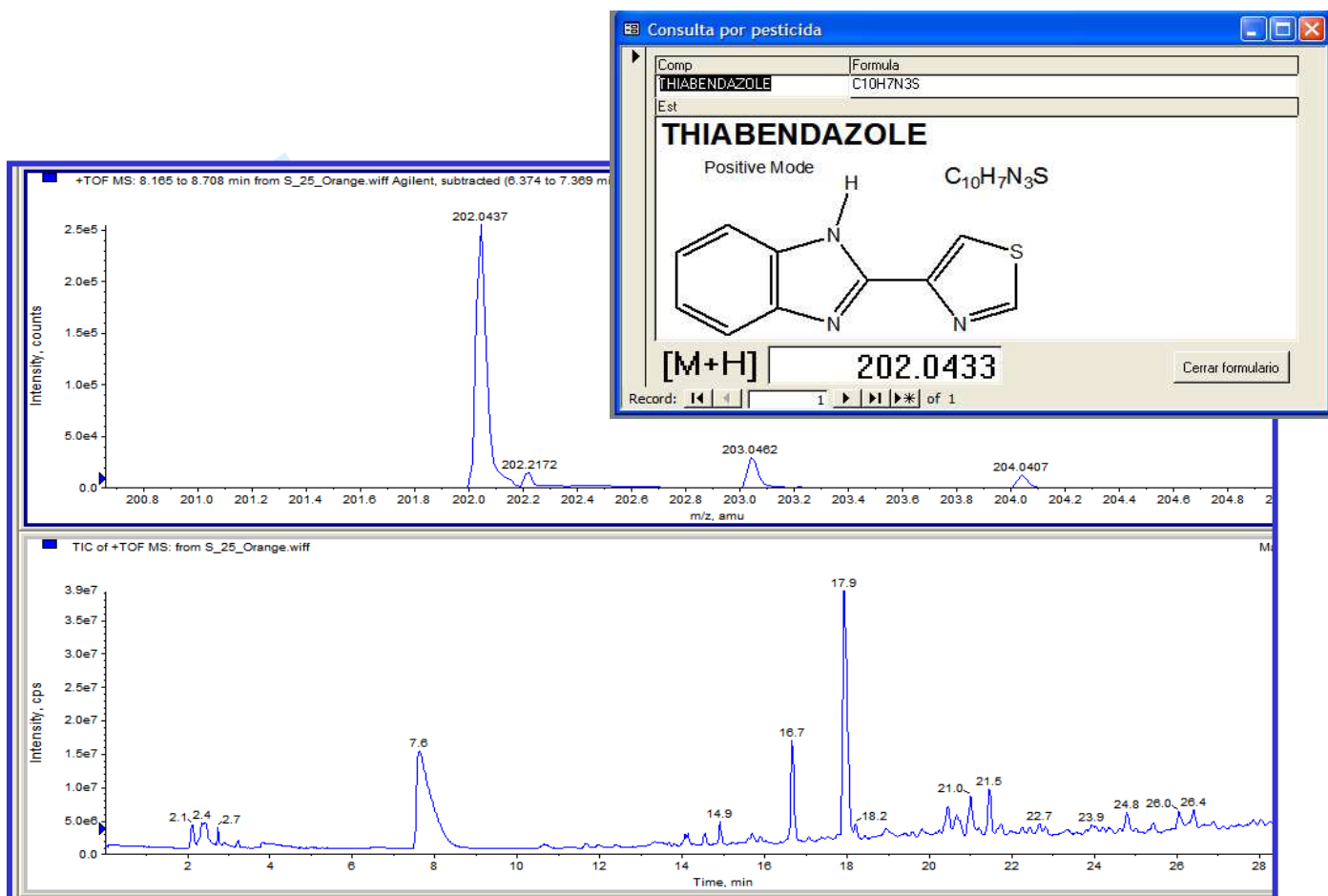


Figure 4. Accurate mass screening for mass of m/z 202.0437.

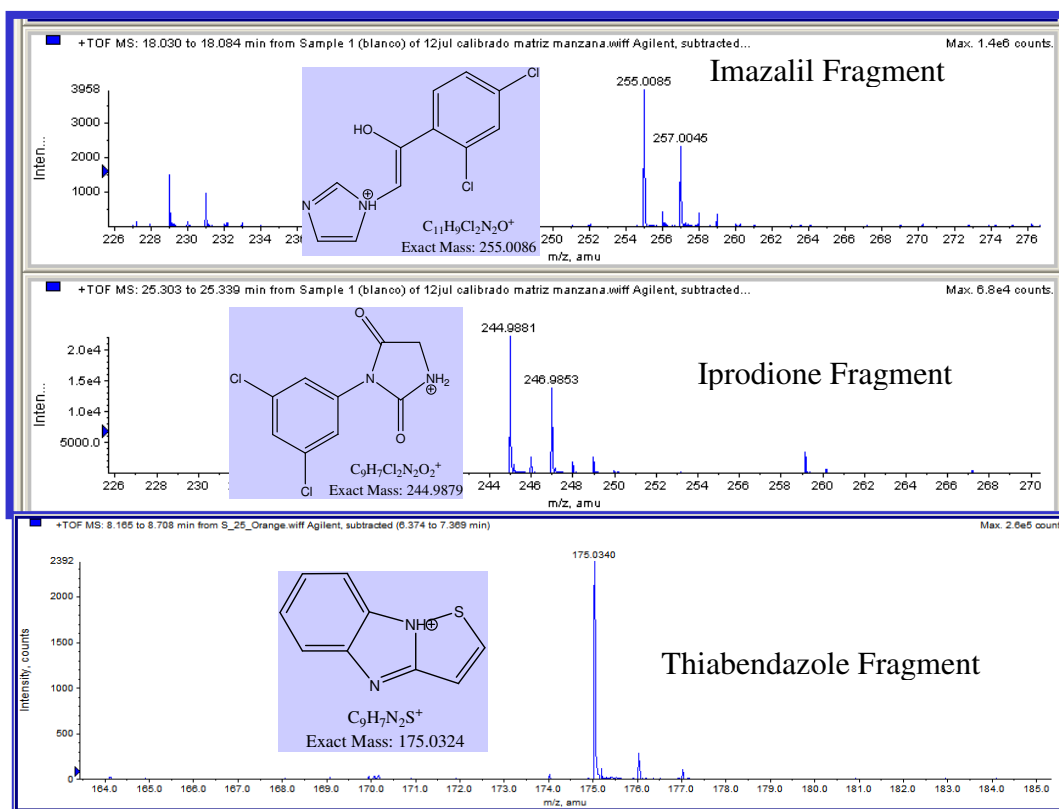


Figure 5. Fragment ions for the three pesticides, imazalil, inrodione, and thiabendazole.

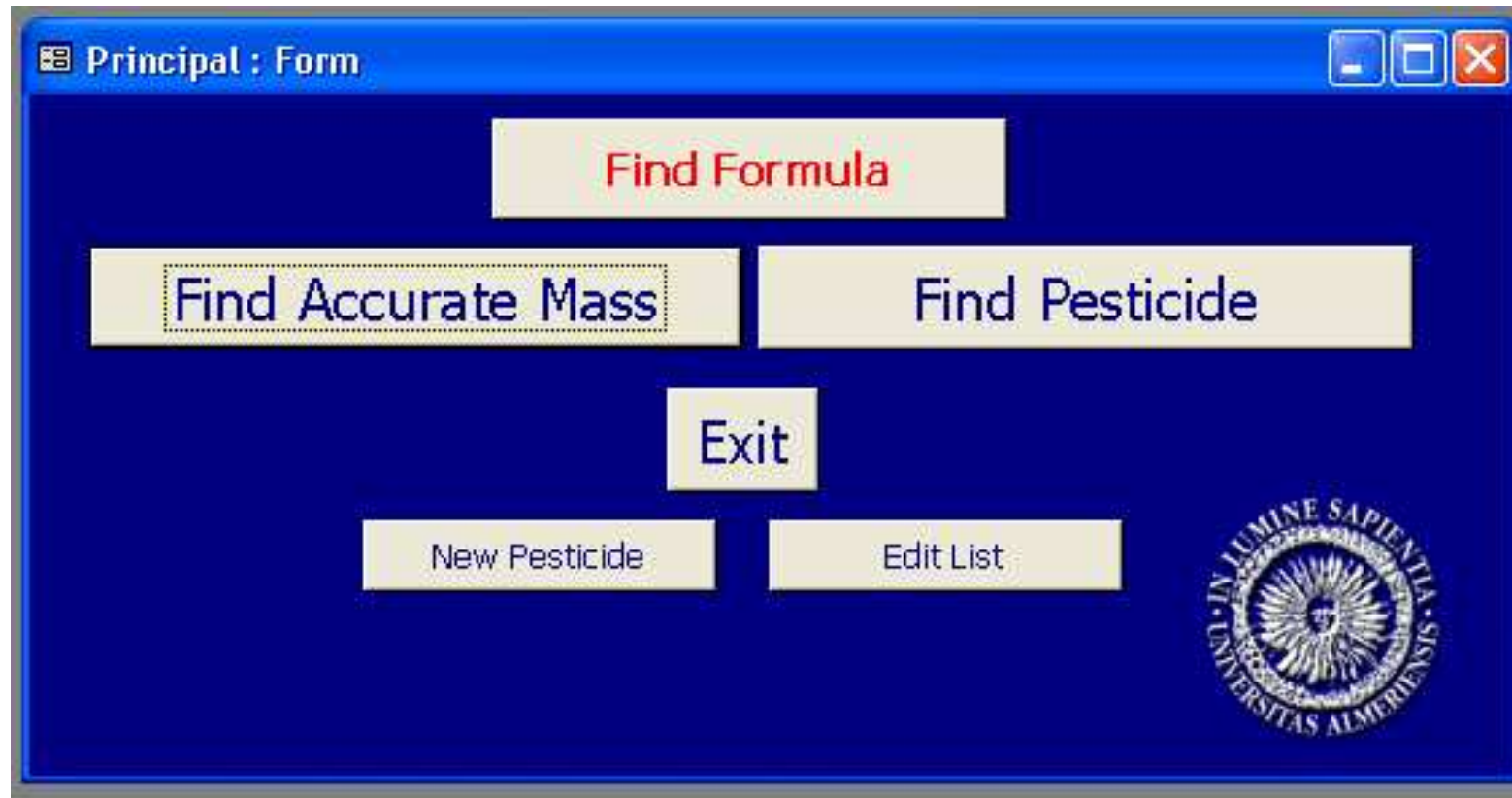


Figure 1. Appearance of the Access Database, called Pesticidas

Table 1. List of 350 Pesticides in “Pesticidas” Database.

Pesticide	Formula	MH+	Pesticide	Formula	MH+
METHAMIDOPHOS	C2H8NO2PS	142.0086	ALDICARB SULFOXIDE	C7H14N2O3S	207.0798
8-Hydroxyquinoline	C9H7NO	146.0600	Isoprotruron	C12H18N2O	207.1492
Phenoxyacetic acid	C8H8O3	153.0546	Quinoclamine	C10H6ClNO2	208.0160
Daminozide	C6H12N2O3	161.0921	PROMECA RB	C12H17NO2	208.1332
Dazomet	C5H10N2S2	163.0358	Aminocarb	C11H16N2O2	209.1285
METHOMYL	C5H10N2O2S	163.0536	PROPOXUR	C11H15NO3	210.1125
Nicotine	C10H14N2	163.1230	Acibenzolar-S-methyl	C8H6N2OS2	210.9994
Fenuron	C9H12N2O	165.1022	Propachlor	C11H14ClNO	212.0837
2-Phenoxypropionic acid	C9H10O3	167.0703	Deethylcyanazine	C7H9ClN6	213.0650
CYROMAZINE	C6H10N6	167.1040	Chlorotoluron	C10H13ClN2O	213.0789
Diphenylamine	C12H11N	170.0964	OMETHOATE	C5H12NO4PS	214.0297
Deethylhydroxyatrazine	C6H11N5O	170.1036	Chlorpropham	C10H12ClNO2	214.0629
Deisopropylatrazine	C5H9N5Cl	174.0541	Simetryn	C8H15N5S	214.1121
Propham	C10H13NO2	180.1019	Deethylterbutryn	C8H15N5S	214.1121
ACEPHATE	C4H10NO3PS	184.0192	MCPA methylester	C10H11ClO3	215.0469
Demethyl monuron	C8H9ClN2O	185.0476	Monolinuron	C9H11ClN2O2	215.0582
Fuberidazole	C11H8N2O	185.0709	Metrubuzin	C8H14N4OS	215.0961
Deethylsimetryne	C6H11N5S	186.0808	ATRAZINE	C8H14ClN5	216.1010
1-Naphthalene acetamide	C12H11NO	186.0913	Cycloate	C11H21NOS	216.1417
Chlorophenoxyacetic acid	C8H7ClO3	187.0156	Terbacil	C9H13ClN2O2	217.0738
1-Naphthaleneacetic acid	C12H10O2	187.0754	THIABENDAZOLE	C10H7N3OS	218.0383
Deethylatrazine	C6H11N5Cl	188.0697	PYMETROZINE	C10H11N5O	218.1036
Molinate	C9H17NO5	188.1104	2,4-D	C8H6Cl2O3	218.9621
PROPAMOCARB	C9H20N2O2	189.1598	Demethylfluometuron	C9H9F3N2O	219.0740
Tricyclazole	C9H7N3S	190.0433	THIOFANOX	C9H18N2O2S	219.1162
EPTC	C9H19NO5	190.1260	OXAMYL	C7H13N3O3S	220.0750
BUTOCARBOXIM	C7H14N2O2S	191.0849	Dichlorvos	C4H7Cl2O4P	220.9532
ALDICARB	C7H14N2O2S	191.0849	QUINMERAC	C11H8ClNO2	222.0316
Clpyralid	C6H8Cl2NO2	191.9614	Chloridazon	C10H8ClN3O	222.0429
CARBENDAZIM	C9H9N3O2	192.0768	Methabenzthiazuron	C10H11N3OS	222.0696
Demethylisoprotruron	C11H16N2O	193.1335	CARBOFURAN	C12H15NO3	222.1125
3,4,5-TRIMETHACARB	C11H15NO2	194.1176	ACETAMIPRID	C10H11N4Cl	223.0745
Hydroxyatrazine	C8H15N5O	198.1349	ALDICARB SULPHONE	C7H14N2O4S	223.0747
Deethylterbutmeton	C8H15N5O	198.1349	BUTOXYCARBOXIM	C7H14N2O4S	223.0747
MCPA	C9H9ClO3	199.0167	ALDOXYCARB	C7H14N2O4S	223.0747
Monuron	C9H11ClN2O	199.0633	Sulfallate	C8H14ClN2S2	224.0329
Cymoxanil	C7H10N4O3	199.0826	Monocrotophos	C7H14NO5P	224.0682
Deisopropylprometryne	C7H13N5S	200.0964	BENDIOCARB	C11H13NO4	224.0917
Deethylametryn	C7H13N5S	200.0964	Mepanipyrim	C14H13N3	224.1182
PYRIMETHANIL	C12H13N3	200.1182	Desmethylpirimicarb	C10H16N4O2	225.1346
MCPA	C9H9ClO3	201.0313	METHIOCARB	C11H15NO2S	226.0896
acetate	C13H12O2	201.0910	ETHIOFENCARB	C11H15NO2S	226.0896
THIABENDAZOLE	C10H7N3OS	202.0433	CYPRODIMINIL	C14H15N3	226.1339
SIMAZINE	C7H12ClN5	202.0854	Terbutmeton	C10H19N5O	226.1662
CARBARYL	C12H11NO2	202.0863	Dichlone	C10H4Cl2O2	226.9661
Fenfuram	C12H11NO2	202.0863	Ametryn	C9H17N5S	228.1277
2-Naphthoxyacetic acid	C12H10O3	203.0703	Metoxuron	C10H13ClN2O2	229.0738
METAMITRON	C10H10NO	203.0927	Tebuthiuron	C9H16N4OS	229.1118
Hormodin	C12H13NO2	204.1019	DIMETHOATE	C5H12NO3PS2	230.0069
Pebulate	C10H21NOS	204.1417	Dicryl	C10H9Cl2NO	230.0134

Pesticide	Formula	MH+	Pesticide	Formula	MH+
Trietazine	C9H16ClN5	230.1167	Diallate	C10H17Cl2NOS	270.0481
TERBUTHYLAZINE	C9H16ClN5	230.1167	Alachlor	C14H20ClNO2	270.1255
Methfuroxam	C14H15NO2	230.1176	5-Hydroxy-imidacloprid	C9H10ClN5O3	272.0545
DEMETON-S-METHYL	C6H15O3PS2	231.0273	Napropamide	C17H21NO2	272.1645
Deethylcyanazine amide	C7H11ClN6O	231.0756	BROMOXYNIL	C7H8Br2NO	273.8508
Deethylcyanazine acid	C7H10ClN6O2	232.0596	Fenpropidin	C19H31N	274.2529
DIURON	C9H10Cl2N2O	233.0243	Anilazine	C9H5Cl3N4	274.9653
Fluometuron	C10H11F3N2O	233.0896	Disulfoton	C8H19O2PS3	275.0358
Dichlorprop	C9H8Cl2O3	234.9923	Neburon	C12H16Cl2N2O	275.0712
2,4-D Methyl ester	C9H8Cl2O3	234.9923	Paraoxon	C10H14NO6P	276.0632
Thiofanox sulfoxide	C9H18N2O3S	235.1111	imazameth	C14H17N3O3	276.1343
Carboxin	C12H13NO2S	236.0740	Phorate sulfone	C7H17O5PS2	277.0328
Fenpiclonil	C11H6Cl2N2	236.9981	2,4-D Butyl ester	C12H14Cl2O2	277.0393
Buturon	C12H13ClN2O	237.0789	Metazachlor	C14H16ClN3O	278.1055
Carbetamide	C12H16N2O3	237.1234	Fenthion	C10H15O3PS2	279.0273
3-Hydroxy Carbofuran	C12H15NO4	238.1074	Oflurace	C14H16ClN3O	282.0891
PIRMICARB	C11H18NO4	239.1503	Propetamphos	C10H20NO4PS	282.0923
Clomazone	C12H14ClNO2	240.0786	Pendimethalin	C13H19N3O4	282.1448
Thiram	C6H12N2S4	240.9956	Dodemorph	C18H35NO	282.2791
Cyanazine	C9H13ClN5	241.0963	Procymidone	C13H11Cl2NO2	284.0240
Prometryne	C10H19N5S	242.1434	FOSTHIAZATE	C9H18NO3PS2	284.0538
Terbutryn	C10H19N5S	242.1434	Penconazole	C13H15Cl2N3	284.0716
Dixanthogen	C6H10O2S4	242.9636	METOLACHLOR	C15H22ClNO2	284.1412
Ethoprophos	C8H19O2PS2	243.0637	VINCLAZOLIN	C12H9Cl2NO3	286.0032
METALAXYL	C15H21NO4	244.1543	Ethofumesate	C13H18O5S	287.0948
Phorate oxygen analogue	C7H17O3PS2	245.0429	Difenoxuron	C16H18N2O3	287.1390
OXY DEMETON-METHYL	C6H15O4PS2	247.0222	VAMIDOTHION	C8H18NO4PS2	288.0488
FLUDIOXONIL	C12H6F2N2O2	247.0324	Cyanofenphos oxygen	C15H14NO3P	288.0784
Paraoxon-methyl	C8H10NO6P	248.0319	Terbufos	C9H21O2PS3	289.0514
LINURON	C9H10Cl2N2O2	249.0192	Myclobutanil	C15H17ClN4	289.1214
Heptenophos	C9H12ClO4P	251.0235	Chloroxuron	C15H15ClN2O2	291.0895
Thiofanox sulfone	C9H18N2O4S	251.1060	Thiamethoxam	C8H10ClN5O3S	292.0266
THIA CLOPRID	C10H9ClN4S	253.0309	Parathion	C10H14NO5PS	292.0403
Hexazinone	C12H20NO2	253.1659	Chlorbromuron	C9H10BrClN2O2	292.9687
2,4,5-T	C8H5Cl3O3	254.9377	Etrinfos	C10H17N2O4PS	293.0719
Fluroxypyr	C7H5Cl2F2NO3	254.9734	Triadimefon	C14H16ClN3O2	294.1004
Propyzamide	C12H11Cl2NO	256.0290	Pacllobutrazol	C15H22ClN3O	294.1368
IMIDACLOPRID	C9H10ClN5O2	256.0596	Folpet	C9H4Cl3NO2S	295.9101
N-m-Tolylphthalamic acid	C15H13NO3	256.0968	Triadimenol	C14H18ClN3O2	296.1160
Dimethachlor	C13H18ClNO2	256.1099	2,4,5-T Isopropyl ester	C11H11Cl3O3	296.9847
Trichlorfon	C4H8Cl3O4P	256.9299	IMAZALIL	C14H14Cl2N2O	297.0556
Metobromuron	C9H11BrN2O2	259.0077	SPIROXAMINE	C11H8Br5NO2	298.2741
Cyanazine amide	C9H15ClN6O	259.1069	Phoxim	C12H15N2O3PS	299.0614
Cyanazine acid	C9H14ClN6O2	260.0909	Quinalphos	C12H15N2O3PS	299.0614
Phorate	C7H17O2PS3	261.0201	Merphos	C12H27PS3	299.1085
Bromacil	C9H13BrN2O2	261.0233	Captan	C9H8Cl3NO2S	299.9414
phorate sulfoxide	C7H17O4PS2	261.0379	Phosphamidon	C10H19ClN5O5P	300.0762
2,4-D Isopropyl ester	C11H12Cl2O3	263.0236	Tolclofos methyl	C9H11Cl2O3PS	300.9616
Parathion-methyl	C8H10NO5PS	264.0090	DESMEDIPHAM	C16H16N2O4	301.1183
aclonifen	C12H9ClN2O3	265.0374	PHENMEDIPHAM	C16H16N2O4	301.1183
Oxycarboxin	C12H13NO4S	268.0638	FENHEXAMID	C14H17Cl2NO2	302.0709
Diethencarb	C14H21NO4	268.1543	Flutriafol	C16H13F2N3O	302.1099
Silvex	C9H7Cl3O3	268.9534	FENOXY CARB	C17H19NO4	302.1387

Table 1. Continued, "Pesticidas" Access Database

Pesticide	Formula	MH+	Pesticide	Formula	MH+
Methidathion	C6H11N2O4PS3	302.9691	Fenbuconazole	C19H17ClN4	337.1214
Clofentezine	C14H8Cl2N4	303.0199	Bitertanol	C20H23N3O2	338.1863
Cyanofenphos	C15H14NO2PS	304.0556	Phenyl mercuric acetate	C8H8HgO2	339.0303
Fenamphos	C13H22NO3PS	304.1131	Dimelfuron	C15H19ClN4O3	339.1218
Fenpropimorph	C20H33NO	304.2635	Pyridaphenthion	C14H17N2O4PS	341.0719
Diazinon	C12H21N2O3PS	305.1083	Bifenox	C14H9Cl2NO5	341.9931
Primiphos-methyl	C11H20N3O3PS	306.1036	Propiconazole	C15H17Cl2N3O2	342.0771
BUPROFEZIN	C16H23N3OS	306.1635	THIOPHANATE-METHYL	C12H14N4O4S2	343.0529
oxamide	C15H15ClN2O3	307.0844	Prothiophos	C11H15Cl2O2PS2	344.9701
Fenazaquin	C20H22N2O	307.1805	Azinphos-ethyl	C12H16N3O3PS2	346.0443
Quinoxifen	C15H8Cl2FNO	308.0040	TRIFLUMIZOLE	C15H15ClF3N3O	346.0928
TEBUCONAZOLE	C16H22ClN3O	308.1524	Isofenphos	C15H24NO4PS	346.1236
DIFLUBENZURON	C14H9ClF2N2O2	309.0248	Tolyfluanid	C10H13Cl2F2N2O2S2	346.9852
Isazofos	C9H17ClN3O3PS	314.0490	Coroxon	C14H16ClO6P	347.0446
Isoxathion	C13H16NO4PS	314.0610	Gibberellic acid	C19H24O6	349.1646
Triazophos	C12H16N3O3PS	314.0723	Clodinafop-Propargyl	C17H13ClFNO4	350.0590
Hexaconazole	C14H17Cl2N3O	314.0821	Fenpropathrin	C22H23NO3	350.1751
Kresoxim-methyl	C18H19NO4	314.1387	Propargite	C19H26O4S	351.1625
Malaoxon	C10H19O7PS	315.0662	Hexythiazox	C17H21ClN2O2S	353.1085
Nuarimol	C17H12ClF2N2O	315.0695	TEBUFENOZIDE	C22H28N2O2	353.2224
Flusilazole	C16H15F2N3Si	316.1076	THIODICARB	C10H18N4O4S3	355.0563
Bupirimate	C13H24N4O3S	317.1642	TRIFLUMURON	C15H10ClF3N2O3	357.0259
Phosmet	C11H12NO4PS2	318.0018	CHLORSULFURON	C12H12ClN5O4S	358.0372
Azinphos-methyl	C10H12N3O3PS2	318.0130	Chlorfenvinphos	C12H14Cl3O4P	358.9768
Triflconazole	C17H20ClN3O	318.1368	OXYFLUORFEN	C15H11ClF3N4	360.0256
Metconazole	C17H22ClN3O	320.1524	FLORASULAM	C12H8F3N5O3S	360.0373
IPROVALICARB	C18H28N2O3	321.2173	CLETHODIM	C17H26ClN3O3S	360.1395
Flamprop	C16H13ClFNO3	322.0641	Haloxifop	C15H11ClF3N4	362.0401
Pyriproxyfen	C20H19NO3	322.1438	Fenoxaprop-ethyl	C18H16ClNO5	362.0790
Sulfotep	C8H20Cl2PS2S2	323.0300	Coumaphos	C14H16ClO6PS	363.0217
Sulprofos	C12H19Cl2PS3	323.0358	Flufenacet	C14H13F4N3O2S	364.0737
EPN	C14H14NO4PS	324.0454	Benzoximate	C18H18ClNO5	364.0946
Azamethiphos	C9H10ClN2O5PS	324.9809	Flamprop-isopropyl	C19H19ClFNO3	364.1110
Diniconazole	C15H17Cl2N3O	326.0821	Tetrachlorvinphos	C10H9Cl4O4P	364.9065
Benalaxyl	C20H23NO3	326.1751	Pyridaben	C19H25ClN2OS	365.1449
ISOXAFLUTOLE	C12H15F3NO4S	327.0747	Dinocap	C18H24Cl2O6	365.1707
Fluazifop acid	C15H12F3NO4	328.0791	Phosalone	C12H15ClNO4PS2	367.9941
Diclobutrazol	C15H19Cl2N3O	328.0978	Methoxyfenozide	C22H28N2O3	369.2173
oxygen	C11H15Cl2O3PS	328.9929	IOXYNIL	C7H32NO	369.8231
Pencycuron	C19H21ClN2O	329.1415	AMIDOSULFURON	C9H15N5O7S2	370.0486
Iprodione	C13H14Cl2N3O3	330.0407	Thiophanate ethyl	C14H18N4O4S2	371.0842
Mecarbam	C10H20NO5PS2	330.0593	TETRACONAZOLE	C13H11Cl2F4N3O	372.0288
Epoxiconazole	C17H13ClF3N3O	330.0804	Profenofos	C11H15BrClO3PS	372.9424
Fluridone	C19H14F3NO	330.1100	QUAZALOFOP-ETHYL	C19H17ClN2O4	373.0950
Dacthal	C10H6ClO4	330.9093	Pyrazophos	C14H20N3O5PS	374.0934
Fenarimol	C17H12Cl2N2O	331.0399	Famoxadone	C22H18N2O4	375.1339
Malathion	C10H19Cl2PS2	331.0433	Phosfon	C20H34Cl2P	375.1770
Dichlofluanid	C9H11Cl2F2N2O2S2	332.9696	Bromuconazole	C13H12BrCl2N3O	375.9614
Flurtamone	C18H14F3NO2	334.1049	Fluquinconazole	C16H8Cl2F2NO	376.0163
Primiphos-ethyl	C13H24N3O3PS	334.1349	Prochloraz	C15H16Cl3N3O2	376.0381
Tebufenpyrad	C18H24ClN3O	334.1681	HALOXYFOP-METHYL	C16H13ClF3N4	376.0558
Flamprop-methyl	C17H15ClFNO3	336.0797	FLAZASULFURON	C13H12F3N5O5	376.0863
Cloquintocet-Mexyl	C18H22ClNO3	336.1361	Clethodim-sulfoxide	C17H26ClNO4S	376.1344

Pesticide	Formula	MH+
Etofenprox	C25H28ClO3	377.2111
Naled	C4H7Br2Cl2O4P	378.7898
Endrin	C12H8Cl6O	378.8779
Dieldrin	C12H8Cl6O	378.8779
PYRIDATE	C19H23ClN2O2S	379.1242
TEFLUBENZURON	C14H6Cl2F4N2O2	380.9815
Carbosulfan	C20H32N2O3S	381.2206
Metsulfuron	C14H15N5O6S	382.0816
FURATHIOCARB	C18H26N2O5S	383.1635
Fluazifop-butyl	C19H20F3NO4	384.1417
Ethion	C9H22O4P2S4	384.9949
Thifensulfuron methyl	C12H13N5O6S2	388.0380
DIMETHOMORPH	C21H22ClNO4	388.1310
Clethodim-sulfon	C17H26ClNO5S	392.1293
Dialfos	C14H17ClNO4PS2	394.0098
Diflufenican	C19H11F5N2O2	395.0813
Rotenone	C23H22O6	395.1489
Tribenuron methyl	C15H17N5O6S	396.0972
TRIASULFURON	C14H16ClN5O5S	402.0633
AZOXYSTROBIN	C22H17N3O5	404.1241
Dfenaconazole	C19H17Cl2N3O3	406.0720
Flazasulfuron	C13H12F3N5O5S	408.0584
Trifloxystrobin	C20H19F3N2O4	409.1370
Bensulfuron-methyl	C16H18N4O7S	411.0969
NICOSULFURON	C15H18N6O6S	411.1081
Benfuracarb	C20H30N2O5S	411.1948
CINOSULFURON	C15H19N5O7S	414.1078
Metosulam	C14H13Cl2N5O4S	418.0138
HALOXYFOP-ETHOXYETHYLESTER	C19H19ClF3NO4	418.1027
PROSULFURON	C15H16F3N5O4S	420.0948
Fenpyroximate	C24H27N3O4	422.2074
RIMSULFURON	C14H17N5O7S2	432.0642
Haloxifop-etotyl	C19H19ClF3NO5	434.0977
HEXAFLUMURON	C16H8Cl2F6N2O3	458.9743
Sulfosulfuron	C19H21N3O7S2	468.0894
Primsulfuron-methyl	C15H12F4N4O7S	469.0436
FLUFENOXURON	C21H11ClF6N2O3	489.0435
Trisulfuron methyl	C17H19F3N6O6S	493.1112
Deltamethrin	C22H19Br2NO3	503.9804
LUFENURON	C17H8Cl2F8N2O3	510.9857
INDOXACARB	C22H17ClF3N3O7	528.0780
Chlorfluazuron	C20H8Cl3F5N3O3	539.9702
Acrinathrin	C26H21F6NO5	542.1397
SPINOSYN A	C41H65NO10	732.4681
SPINOSYN D	C42H67NO10	746.4838
Avermectin B1b	C47H70O14	859.4844
Avermectin B1a	C48H72O14	873.5000

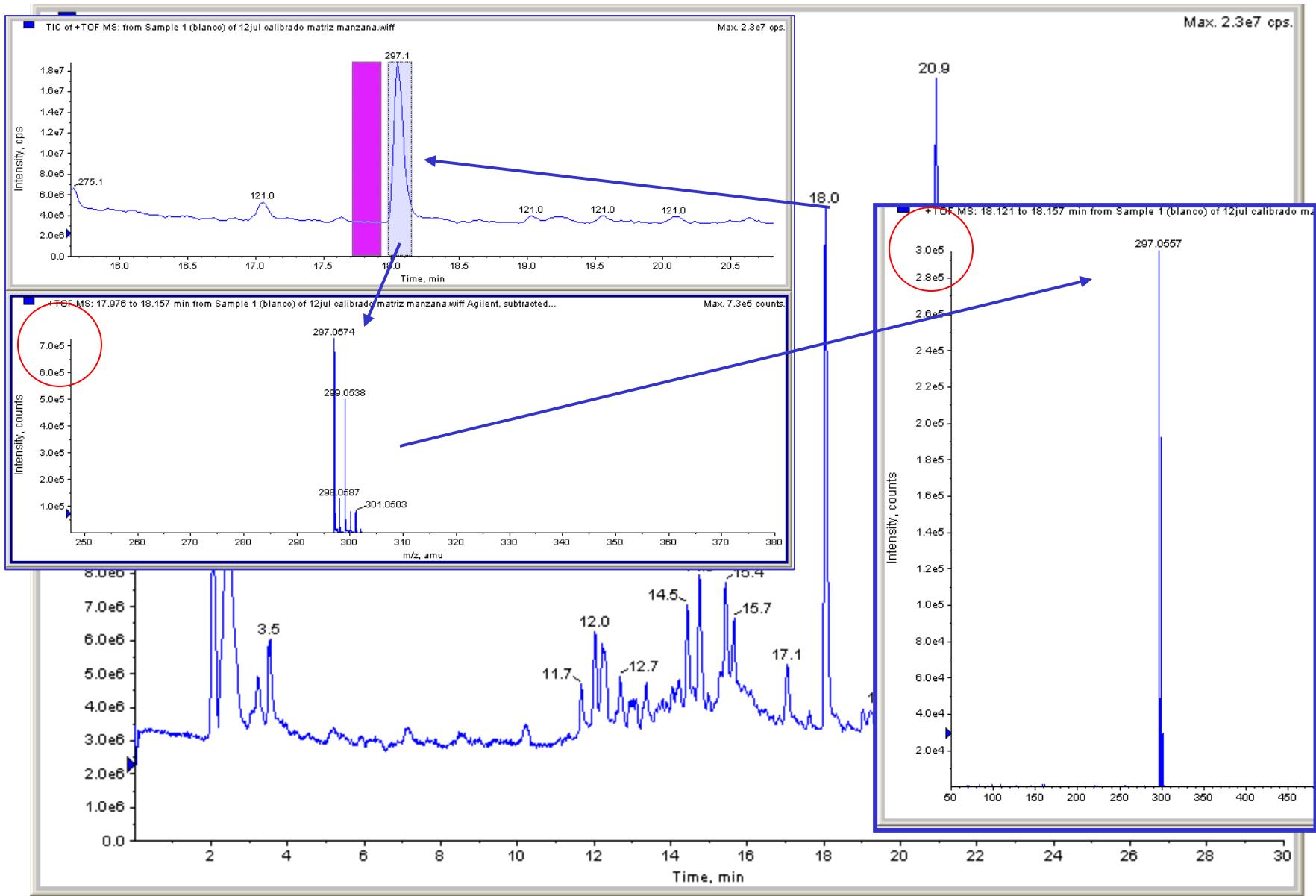


Figure 2. Total ion chromatogram of apple extract using LC/TOFMS.

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Principal : Form

Find Formula

Find Accurate Mass

Find Pesticide

Exit

New Pesticide

Edit List

Enter Parameter Value

Mass

297.0574

OK Cancel

Find Pesticide

Comp	Formula	Est	MH	Cer
▶ IMAZALIL	C14H14Cl2N2O		297.06	
*			0	

IMAZALIL

Positive Mode

$C_{14}H_{14}Cl_2N_2O$

Clc1ccc(cc1C2=CN=CN2)C(=O)OCC=C

[M+H] 297.0556

Record: 1 of 1

Figure 3. Access database search for accurate mass of the m/z 297.0574 ion.

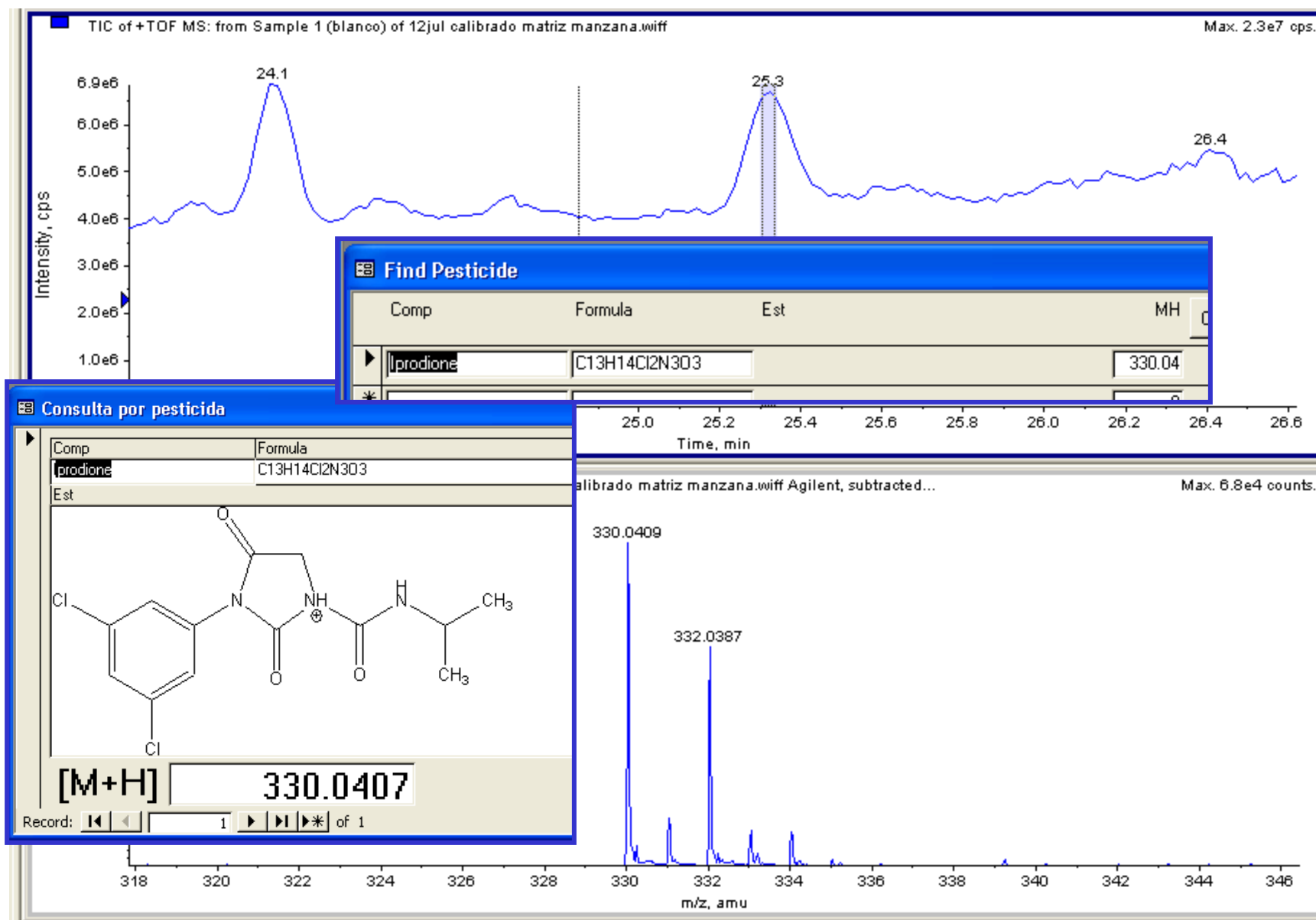


Figure 4. Accurate mass screening for mass of m/z 330.0409.

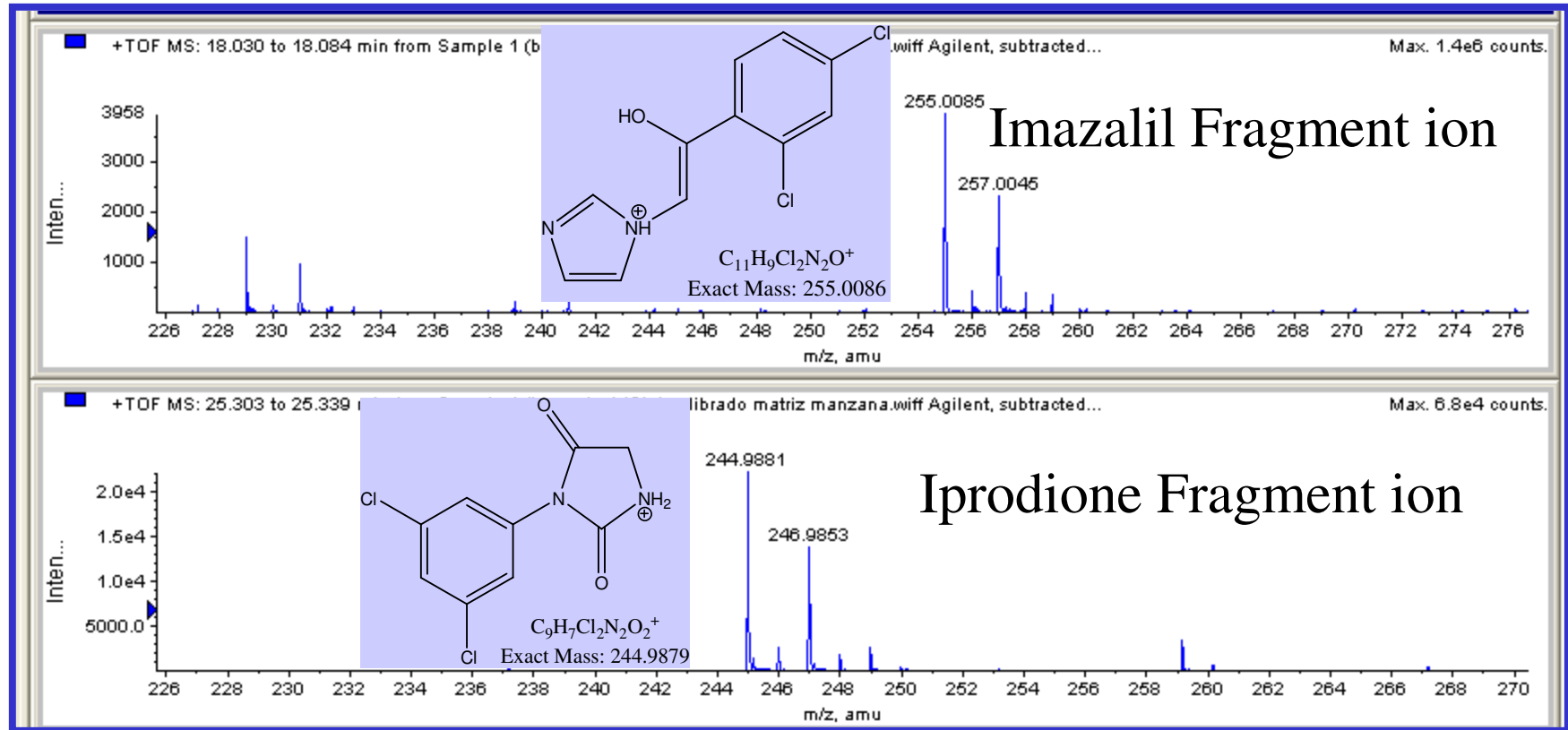


Figure 5. Fragment ions for the two pesticides, imazalil and iprodione with accurate masses and structural assignments.