Chemical Characterization of Neonicotinoids:Imidacloprid and Chlothianidin by gas chtomatography coupled to mass spectrometry (GC/MS)

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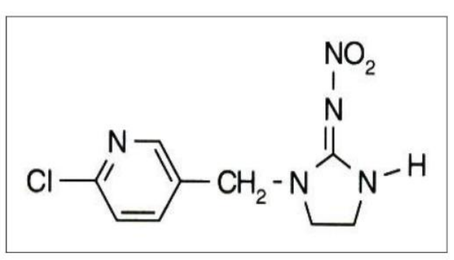
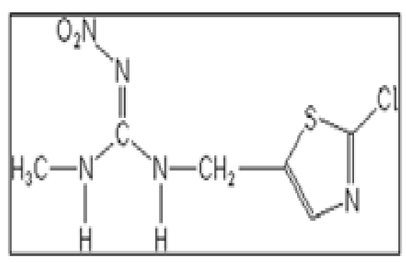
INTRODUCTION

Recently, several reports have been published discussing reduction in bee population which polymerizes cultures around the world, this phenomenon is known as Colony Collapse Disorder (CCD). The phenomenon describes the lack of worker honeybees in the colony despite having pups and food[1]. The causes of this problem is unknown but there are studies that claim that reduction of population of bees is linked to poisoning through insecticide specifically neonicotinoids. Among this type of pesticide are imidacloprid and clothianidin.This paper presents the qualitative analysis of neonicotinoids - clothianidin and imidacloprid - by the technique of gas chromatography coupled to mass spectrometry (GC/MS).





INSTRUMENTATION AND CHROMATOGRAPHIC CONDITIONS

Methodology: The samples are diluted with acetonitrile for analysis of organic compounds.

Instrumental analysis: A GC/MS Shimatzu, model QP5000 equiped with a 30 m DB5 capillary column with internal diameter of 0.25 µm film thicknee was used. Helium was used as carrier gas and gave a column head pressure of 12 p.s.i. and a average flux of 1 mL/min. One microliter of sample was injected into the gas chromatograph containing 100 $mg.L^{-1}$, the injection mode was split-less, the DB-5 column temperature program was as follows: 80 °C isotherm during one minute, ramp temperature of 40 °C/min till 270 °C, isothermal during 5 minutes, ramp 10 °C per minute up to 280 °C and finally isothermal during 2 minutes. The analysis on the mass spectrometer was performed in scan mode from mass 50 until 300 m/z.

RESULTS AND DISCUSSION

In order to acquired, and concentrated at 1mL of each extract were injected and analyzed by GC/MS. Four chromatograms for each extract were obtained. Figure 1 show the chromatogram of Imidacloprid, this analyte elute within retention time of 8.2 minutes. Figure 2 show the mass spectrum of this specific retention time and with a NIST library search match the Imidacloprid chemical compound.

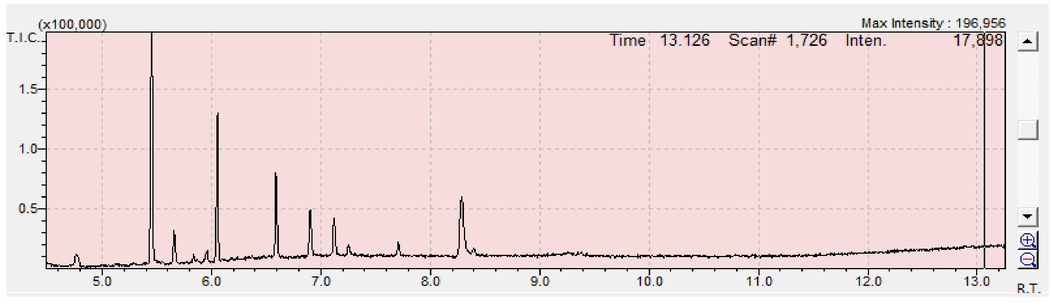


Figure 1: Chromatogram of Imidacloprid with Retention Time of 8.2 minutes.

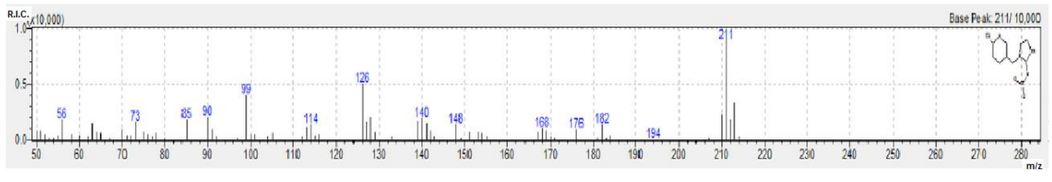


Figure 2: Mass spectrum of Imidacloprid

The mass spectrum of the Imidacloprid with chemical formula $C_9H_{10}ClN_5O_2$, shows that the molecule is unstable in the ion source with electron impact of 70 eV due to no presence of ion molecule m/z 255. The fragment ion $C_6H_5ClN^+$ m/z 126 is well depicted in the mass spectrum. The m/z 211 can be explained by the nitrogen rule as follow: First the Imidacloprid ion molecule loose NO_2 due this fact the molecule has to be rearrange. To this ion turn stable a rearrange between C=N has to carry on. Double link will form between two carbons and this fact will liberated two hydrogen, these two hydrogen free atoms will link into nitrogen atom to stabilized the molecule within mass m/z 211, this mass is well depict in the Imidacloprid mass spectrum in figure 2.

Figure 3 shows the chromatogram of clothianidin, this analyte elute within retention time of 7.3 minutes. The mass spectrum of the clothianidin with chemical formula $C_6H_8ClN_5O_2S$ represent in Figure 5, shows that the molecule (Figure 6) is unstable in the ion source with electron impact of 70 eV due to no presence of ion molecule m/z 255. The fragment ion $C_4H_3ClSN^+$ m/z 132 is well depicted in the mass spectrum. The m/z: 170 and 205 might be a fragment ion and a rearrange ion, respectively by the nitrogen law. The mass spectrum in Figure 5 is not the NIST search due to have not fit any of mass spectra, in this case it has to develop a new mass spectrum specific for the molecule of clothianidin.

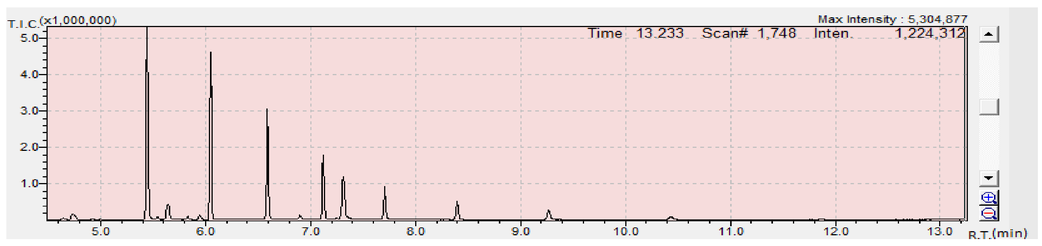


Figure 3: Chromatogram of Clothianidin with Retention Time of 7.3 minutes

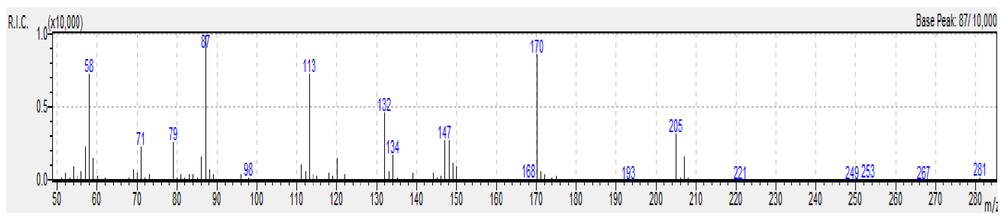


Figure 4: Mass spectrum of Clothianidin

CONCLUSION

This work presents the analysis of clothianidin and imidacloprida by GC/MS within concentration of 100 mg L^{-1}. The clothianidin and imidacloprid, eluted with retention times of 7.3 and 8.2 minutes, respectively. The mass spectrum of imidacloprid was compared with the NIST library of spectra obtained 90% accuracy. In the case of clothianidin, it was not possible to find the spectrum in the library since this is not present in the spectra of the NIST database.

REFERENCES

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