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RAPID SAMPLE COLLECTION SYSTEM FOR ACTIVE MONITORING OF ATMOSPHERIC CONTAMINANTS IN AGRICULTURAL REGIONS

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Abstract: Air pollution is one of the main environmental and public health problems worldwide. In order to measure and evaluate air quality in a region, it is essential to have appropriate systems, networks and programs for this task. The province of Córdoba, Argentina, has a high agricultural/livestock production capacity and agrochemicals are one of its main inputs. Among them, pesticides, which are characterized by presenting a certain degree of toxicity, can contaminate the atmosphere; for this reason, their use must be controlled. Active monitoring systems for atmospheric pollutants currently used in agricultural applications require a sample collection time of 24 hours. The rapid sample collection prototype developed at LIADE uses a brushless motor mounted on a convergent-divergent nozzle to pump, at high speed, a known volume of air through an activated carbon adsorption filter that retains the contaminants present in the circulated air. The qualitative determination of the contaminants retained in the filter is carried out by Gas Chromatography/Mass Spectrometry. For sampling times of 5 minutes, the results of the tests carried out with chlorpyrifos indicated a 70% coincidence with the standard spectrum of the NIST library. The developed system allows to significantly reduce the sample collection time for active monitoring of atmospheric contaminants and makes it possible, for example, to carry out aerial observations in a particular agricultural area to detect the presence of unwanted pesticides in it.

Keywords: Speed, detection, atmospheric pollutants, agricultural region.

INTRODUCTION

Air pollution can be defined as the presence in this medium of solid, liquid and gaseous particles that are harmful to living beings and the environment [1]. It is a phenomenon inherent to the economic, population and technological state of a country and is one of the problems with the greatest difficulty in preventing, evaluating, regulating and controlling, among other causes, due to the multiple emission sources, transformation of pollutants in the atmosphere and the way in which these affect the health of people and ecosystems.

The Province of Córdoba, like other regions of our country, has large areas with a high potential for agricultural and/or livestock production capacity; in them, chemical products for agricultural use, including pesticides and herbicides, constitute one of the main inputs used in agricultural production.

Chemical pesticides and herbicides (phytosanitary and dormant) are characterized by presenting a certain degree of toxicity, which is why it is essential to have systems that allow their presence to be detected, for example in the air, and their concentration to be measured.

Atmospheric monitoring involves the taking of samples (sampling) as well as the analysis of the same. Among the various sampling methods is the so-called active sampling method, used for the detection of both gases and particles. The procedure consists of forcing, during a set period of time, the passage of a known volume of the air under study through a collector formed by a physical medium, such as a filter, or by a chemical solution; the samples of contaminants are retained in the collector and sent to a laboratory for further analysis. In this method, additional volumes of sampled air increase its sensitivity. Most of the equipment that uses this method obtains average daily measurements [2].

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Consequently, the active monitoring systems of atmospheric contaminants that are currently used in agricultural applications require a sample collection time of 24 hours.

This work shows that it is feasible to reduce this 24-hour period to an interval of 1 hour or less, and still retain the ability to qualitatively assess air quality in a given area by identifying pesticides that may exist in the monitored area.

DEVELOPMENT

Monitoring systems that work with active sampling can be low volume (flow rates up to 20-25 l/min) [3] or high volume (flow rates up to 280 l/min) [4],

The prototype built can work with flow rates from 1000 l/min to 2100 l/min.

This was achieved by pumping air into a convergent-divergent nozzle (see figure 1) in whose throat the sample collector was installed.

To ensure a laminar flow of the air mass circulating through the throat, the nozzle was designed according to the requirements of ISO 9300 [5] which specifies the geometry and method of use (installation in a system and operating conditions) of critical flow Venturi nozzles used to determine the mass flow rate of a gas flowing through a system, provides the information necessary to calculate the flow rate and its associated uncertainty, and is applicable to Venturi nozzles in which the gas flow is accelerated to the critical velocity in the throat where the gas mass flow rate is the maximum possible.

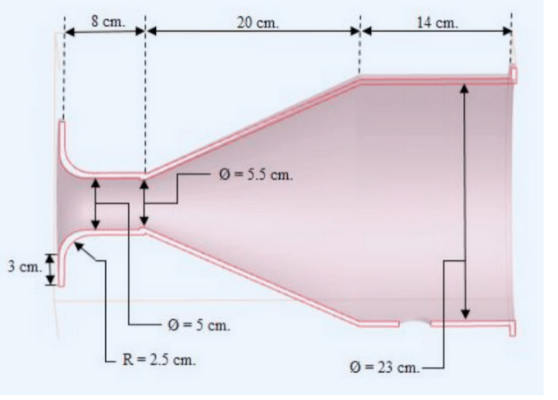

Figure 1: Convergent-divergent nozzle sizing according to ISO 9300 standard.

The designed nozzle was built using 3D printing techniques with a material called PLA, a biodegradable polylactic acid that does not emit harmful gases. In addition, the color white was chosen to print the prototype, since it is a device that is placed outside at the time of monitoring; the selected color prevents ultraviolet radiation from damaging the measuring device (see figure 2).

Figure 2: Nozzle built using 3D printing techniques with white polylactic acid material.

To propel the air into the nozzle, a 20 cm diameter propeller (2 blades) was used, mounted on the shaft of a HD-3536 brushless electric motor with Kv (RPM/V): 1520 RPM/V (see figure 3).

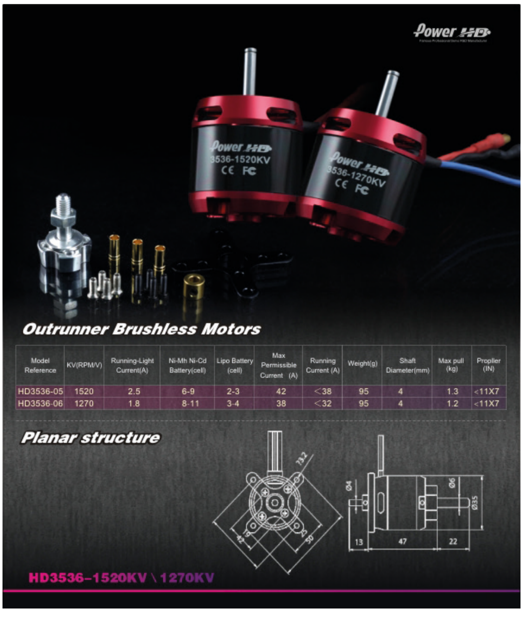

Figure 3: HD3536-1520Kv/1270Kv brushless electric motor datasheet [6].

The motor is powered by a PWM signal that regulates the average input voltage, thus changing its rotation speed and enabling the variation of the air flow. This is achieved by using a HOBBYWING SKYWALKER Airplane 50A UBEC Brushless Speed Controller.

The diameter of the propeller (smaller size available in the local market) was a serious limitation for the design and construction of the convergent-divergent nozzle, since it directly affects the formulas applied for its construction and determines the diameter of the throat [5] and, in turn, the latter sets the diameter of the sample collector to be used.

A 500 ml borosilicate glass tube (better known by the trade names DURAN, Pyrex or Kimax) was used to construct the sample collector, since its dimensions match the measurements proposed for the throat area, and it has desirable physical properties, such as durability and chemical and heat resistance. It is also a viable option, of moderate cost and easily found on the market, as these instruments are widely used in chemical and engineering application laboratories.

The dimensions of the tube make it impossible to distribute the selected adsorbent material, activated carbon in this case, similar to that used by commercial adsorbent tubes. In addition, the quantity of activated carbon needed would be significant, which would make the prototype of the adsorbent tube expensive and difficult to handle. For this reason, it was decided to manufacture discs with a diameter equal to the internal diameter of the glass tube, around which two layers of fabric (lycra and tulle) are sewn, forming a kind of bag inside the disc where the adsorbent material is placed. These filters are then sewn inside an aluminum wire tube (mosquito net). The filters are placed around the support at an approximate angle of 45°-60°, increasing the impact area of the air monitored with the adsorbent material (see figure 4).

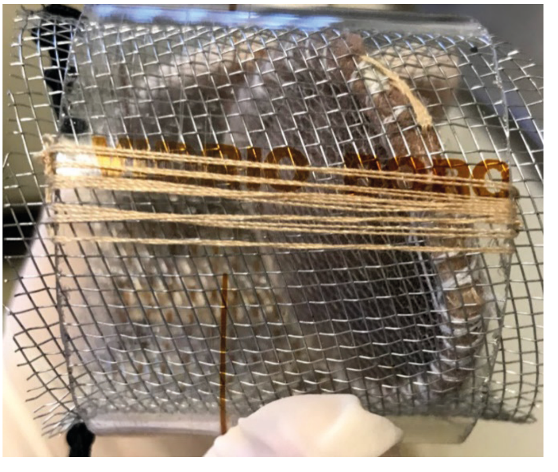

Figure 4: Filter arrangement inside the aluminum wire tube.

The support with the filters, filled with activated carbon, is placed inside the borosilicate glass tube, where the external surface of the support is ensured to coincide entirely with the internal surface of the glass tube (see figure 5).

Figure 5: Prototype of the adsorbent tube ready for use.

To determine the flow rate, a hot wire thermal mass flow meter was used since it is a multivariable sensor (it allows measuring the mass flow rate and the temperature of the fluid); it performs direct measurement of the mass flow rate (it does not require pressure or temperature compensation); and it has no moving parts.

The mass air flow (MAF) sensor selected was the Hellux MAF Sensor, Toyota Corolla 1.6-1.8 Vvti Rav4 3.0 which has an analog voltage output, which represents the value of the air mass flow measured by the sensor.

Integrated into the MAF housing is the temperature sensor (IAT), which works simultaneously with the MAF. Like the MAF sensor, the output signal of the IAT sensor is an analog signal from which the ambient temperature value expressed in °C is obtained.

The Hellux MAF sensor is characterized by a robust structure, which reduces the exposure of sensors, such as the ambient temperature sensor, to dust particles and other dirt, thus reducing contamination of the sensors, and improving detection accuracy and extending the life of the sensor (see figure 6).

Figure 6: Hellux MAF Sensor.

The entire system is controlled by an Arduino MEGA 2560 board and Arduino 1.8.5 software.

The system's power supply is independent and is achieved with a HRB RC Battery 11.1V 5000 mAh 50C-100C 3S LiPo type battery.

Below you can see the prototype for rapid sample collection (see figure 7).

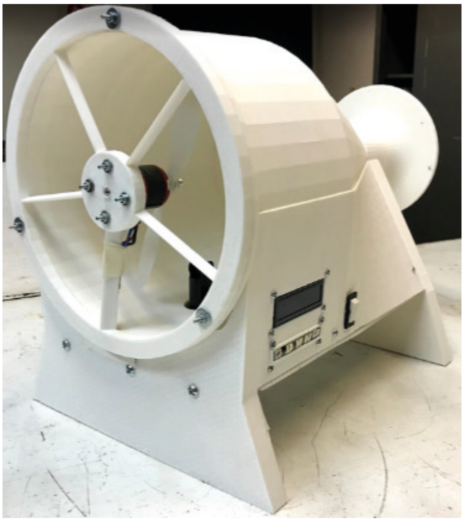

Figure 7: Rapid sample collection prototype.

To verify the capabilities of the rapid sample collection system for active monitoring of atmospheric pollutants, sampling tests were carried out on atmospheres contaminated with Chlorpyrifos (Chlorpyrifos. O-diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate) [7] which is a crystalline non-systemic organophosphate insecticide that can enter the atmosphere through direct application to crops, fields, domestic animals, homes and workplaces. It

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can also enter through volatilization of spills and disposal of waste.

This insecticide was selected for the experiments because, according to the Environmental Protection Agency (EPA) [8], it is one of the most widely used organophosphate insecticides in agriculture. It is used in pest control in the production of fruits, vegetables, cereals and ornamental plants. Its application represents a high environmental impact, hence the importance of its early detection in the air of a given region.

The contaminated atmosphere was simulated in a laboratory, inside an extraction hood.

The qualitative determination of the contaminant present in the air of the hood was carried out by analysis using Gas Chromatography / Mass Spectrometry, after extraction, by thermal desorption, of the samples collected by the activated carbon filter.

RESULTS

Once the prototype was designed and built, the MAF sensors were characterised(see figure 8) and IAT (see figure 9).

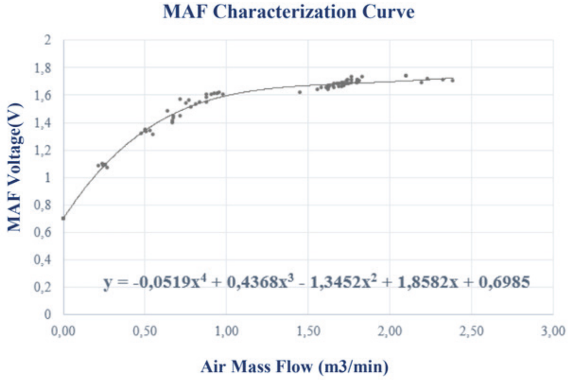

Figure 8: MAF sensor characterization curve.

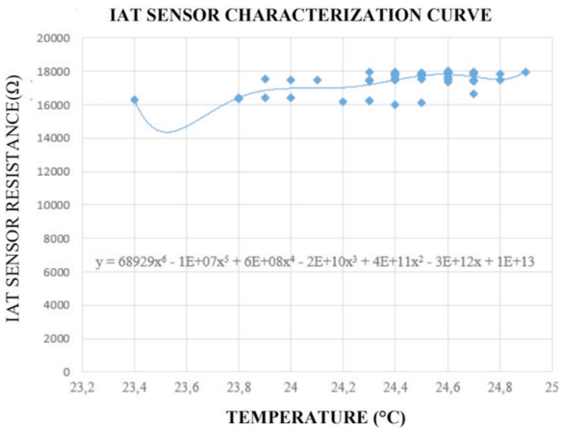

Figure 9: IAT sensor characterization curve.

Once the characterization of the sensors was completed, functional tests were carried out to verify whether it is feasible to perform the qualitative determination of chlorpyrifos present in the monitored air from the samples collected by the constructed system (see figure 10).

Figure 10: Application of the pesticide to be detected in the hood air.

Samples were taken with a collection time of 5 minutes each. New adsorption filters were used in each of them.

Once the sample desorption process was completed, a qualitative analysis of the chlorpyrifos they may contain was carried out using the Gas Chromatography/Mass Spectrometry technique according to the following details:

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- An EPA methodology, method 527, was taken as a reference.
- Eppendorf-dried samples were re-suspended in 100 µL of hexane.
- 1 µL of solution was injected into the GCMS equipment under the following conditions:
- Injector: 250°C.
- Flow: 1mL/min.
- Oven: 55°C x 0 min.

- 20°C/min up to 200°C.

- Hold: 2 min

- 4°C/min up to 300°C.

- Hold: 0.75 min.

- Total time: 35 min.
- MS: Solvent Cut: 5 min. m/: 50-400.

Below is the chromatogram of sample 1 (see figure 11), followed by an image where the area of interest is enlarged (see figure 12), and finally a comparison of the mass spectrum of sample 1 and the spectrum of the NIST library (in Blue: Spectrum of the library, in Red: Spectrum of the chromatogram of sample 1) (see figure 13).

The observed fragments (m/z) are in agreement with those expected in the library. The percentage of agreement between the mass spectrum of sample 1 and the spectrum of the NIST library was 70%.

The observed difference may be due to the low intensity of the signal and the noise existing in the studied area of the chromatogram. However, with these results it can be stated that the sample collection system developed for the active monitoring of atmospheric pollutants in agricultural areas allows to qualitatively determine the presence of pesticides in the air covering these regions.

CONCLUSIONS

The prototype designed and built at LIADE drastically reduces the sampling time for active monitoring of atmospheric pollutants, since it can collect the sample in a period of around tens of minutes, a very short period, in contrast to the twenty-four hours needed by traditional equipment that performs this task.

The use of this system in air quality measurements allows for the rapid and simple detection of contaminants that may be present in the air and for a qualitative determination of them.

The device's independent power supply (batteries) makes it suitable for transport to agricultural areas in order to observe the air above them; this feature, combined with the short sampling time, makes the device an excellent tool for early detection of the presence of unwanted pesticides in these areas.

Reducing the size of the equipment would enable it to be mounted on an Unmanned Aerial Vehicle (UAV) with the aim of carrying out aerial observations of the atmosphere over different agricultural regions.

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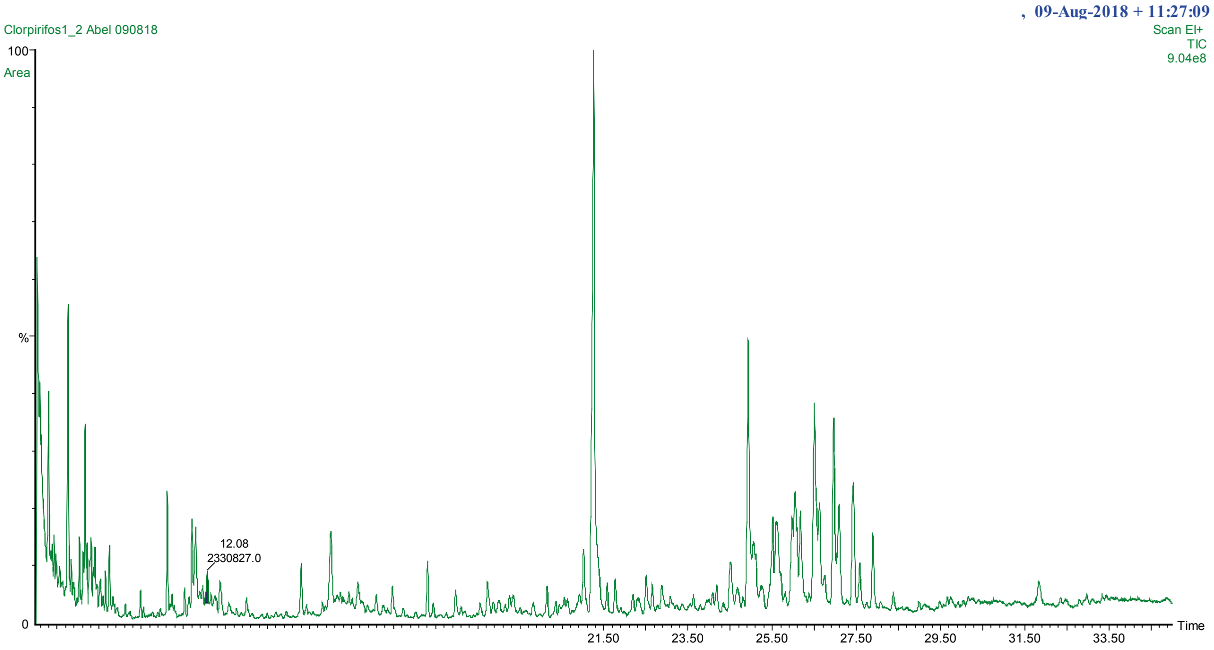

Figure 11: Chromatogram of sample 1.

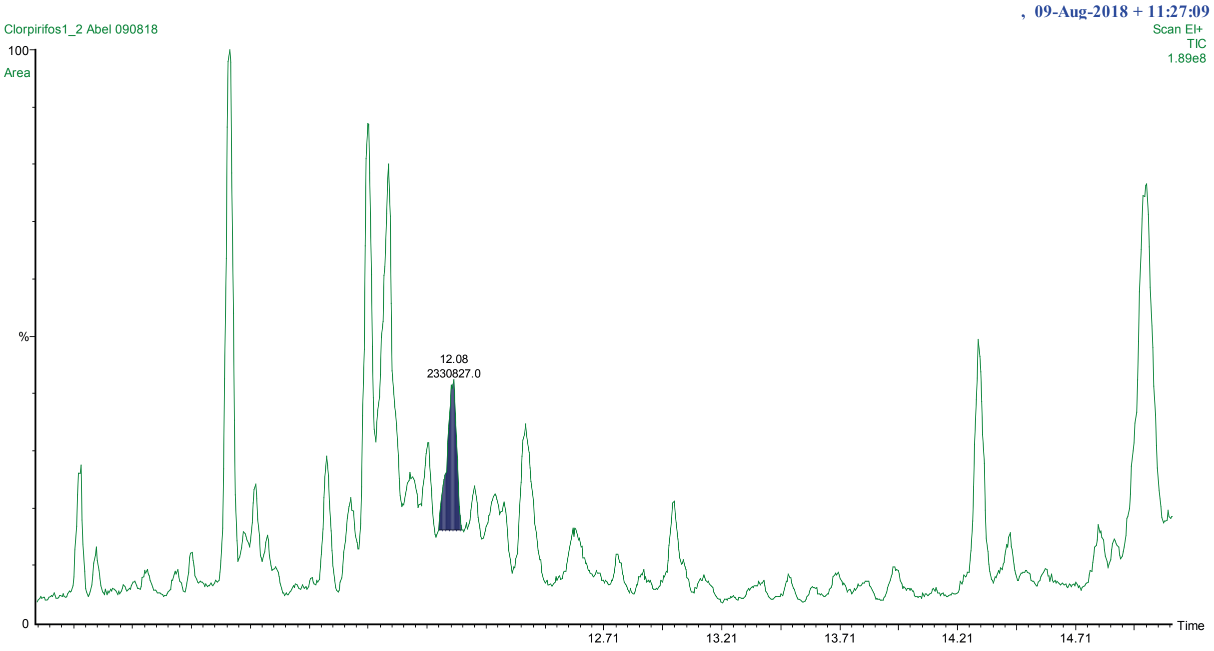

Figure 12: Zooming in on the area of interest of the chromatogram of sample 1.

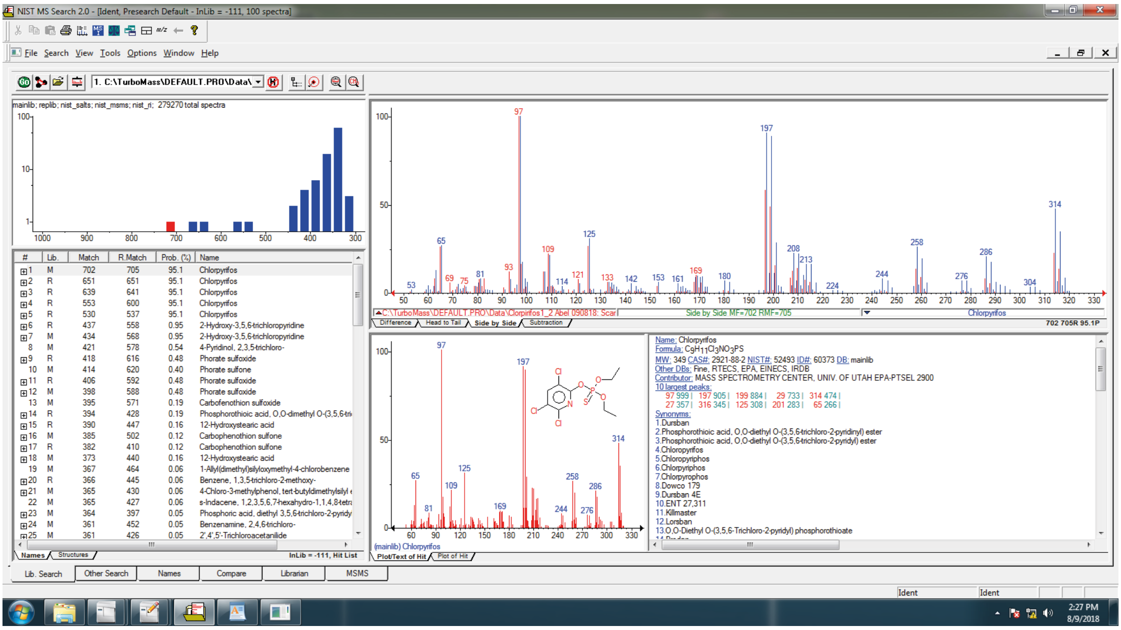

Figure 12: Zooming in on the area of interest of the chromatogram of sample 1.

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