Gas chromatography made cheaper

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Gas chromatography made cheaper

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Abstract :

We describe the assembly of a gas-phase chromatograph that can be constructed by students. This device is very cost-effective, using readily available components from the internet. It operates at low energy consumption (working at room temperature) and utilizes air as the carrier gas. It can be used to introduce students to gas-phase chromatography and can separate mixtures of gases or liquids with boiling points below 150°C at atmospheric pressure. An example of its use is provided to study the quantification of methanol in alcoholic beverages

KEYWORDS :gas chromatography ,Methaol ,Ethanol , alcoholic beverage , Arduino , MQ3 sensor , SnO2

Table of contents

0 - SCOPE OF THE PROJECT
1 - THE DANGERS OF METHANOL IN ALCOHOLIC BEVERAGES
2 - MEASURING METHANOL IN ETHANOL
3 - INTRODUCTION TO THE GAS CHROMATOGRAPH
    3-1 THE MQ3 MEASUREMENT SENSOR
    3-2 THE CARRIER GAS
    3-3 THE INJECTION SYSTEM
    3-4 THE COLUMN
    3-5 CHROMATOGRAM VISUALIZATION

4 DEVELOPING A METHANOL/ETHANOL QUANTIFICATION METHOD
    4-1 SUPPORT SELECTION
    4-2 COMPARISON OF DIFFERENT SPIRITS
    4-3 REPLACEMENT OF THE CARRIER GAS
    4-4 ETHANOL QUANTIFICATION IN FERMENTATION BROTH
    4-5 SOLID-PHASE EXTRACTION

5 LIMITATIONS OF THE CHROMATOGRAPH

BIBLIOGRAPHY

0-SCOPE OF THE PROJECT

Nowadays gas chromatography is a widely used technique to separate various chemical species in a complex mixture. It involves injecting the mixture under study at the head of a column filled with an inert support, which is swept by an inert gas as well (figure 1). Due to differences in their chemical structure, the various compounds present do not progress at the same rate within the column and exit one after the other at the column's outlet. Compounds with the least affinity for the support exit first, and those with the highest affinity exit last .

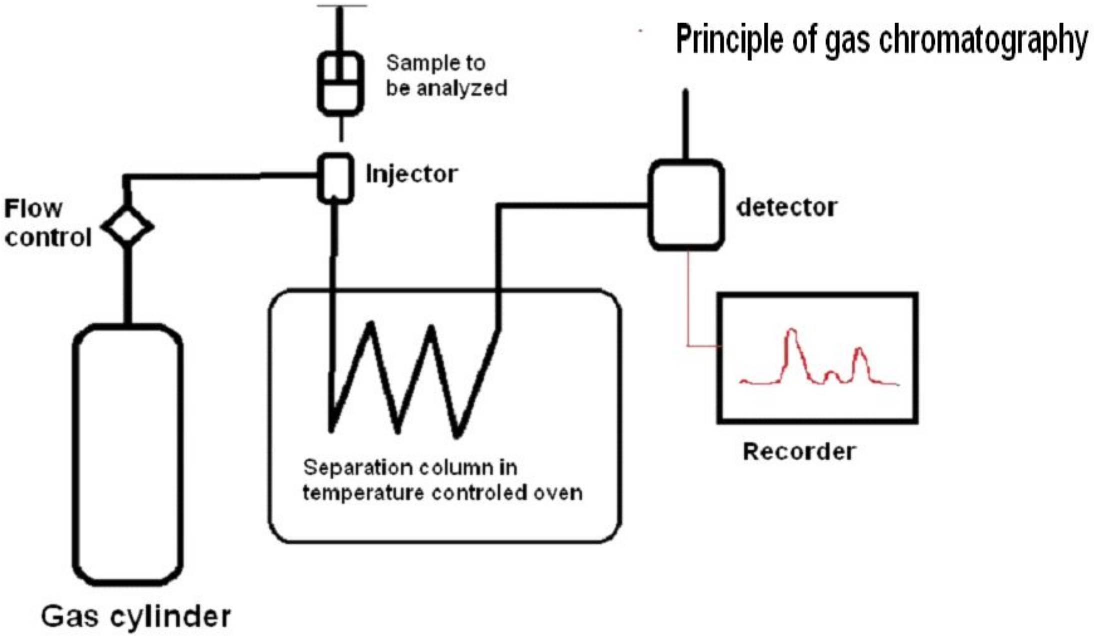


Figure 1

This technique emerged around 1950. The initial users built their own devices, but commercial companies quickly took over their production (ref 0). Nowadays, companies like Varian, Hewlett Packard, Shimadzu, etc., dominate the market (figure 2) . There were a few French companies present at the beginning, such as Girdel, but they disappeared quickly.

While the principle of separation has remained unchanged, there have been many innovations in the detection systems to reveal the presence of the products at the column's outlet. The early devices primarily used thermal conductivity detection. Nowadays, this technique is still used, but others have emerged, such as flame ionization detection, electron capture detection, mass spectrometry, flame photometry, and many others .

Over the years, the devices have become more complex, and their prices haven't really decreased. For a new entry-level device today, you can expect to pay around 20,000 euros. There is an active second-hand market, especially in the USA, where you can purchase relatively recent devices in a price range of 3,000 to 8,000 euros. On auction websites, you can find "vintage" chromatographs in working condition starting from 300 euros. In addition to these prices, you need to consider the cost of supplies and maintenance. Most devices consume hydrogen or helium, which are supplied in high-pressure steel cylinders. Also, don't forget the electricity consumption, typically around 1000 watts at 220 volts.

Commercial gaz chromatograph

Figure 2

The device we are going to present has a significantly lower cost (approximately 20 euros). To visualize the chromatograms, you can use a standard PC or a standalone system based on a microcontroller like "ARDUINO." To top it off, this chromatograph uses air as the carrier gas, so there's no need to provide hydrogen or helium cylinders. It is battery-powered, and its operational consumption does not exceed 2 watts at a voltage of around 12 volts.

The origin of this project stems from a request by an artisanal distiller in the southwest of France who wanted to ensure that the products of their various fruit fermentations (plums, pears, apples, cherries) resulted in a brandy with as little methanol as possible.

Furthermore, this device provides a simple and cost-effective way to get started with gas chromatography using non-hazardous materials.

1 - THE DANGERS OF METHANOL IN ALCOHOLIC BEVERAGES

Periodically, the media reports cases of intoxication caused by the consumption of alcoholic beverages containing methanol. To mention just a few recent incidents, we remember the dozens of deaths in the Czech Republic and Poland in August 2012, the 16 deaths in Indonesia during the New Year's Eve of 2014. The most severe incidents occurred in Libya in March 2013, where the city of Tripoli alone recorded 79 deaths and 879 cases of intoxication. Closer to home, we recall the scandal of Italian wine contaminated with methanol in March 1986, which resulted in the death of 23 people. In this last case, it was producers in southern Italy who, in order to receive European Union subsidies, increased the alcohol content of a wine intended for industrial use. This wine was then intercepted by criminal networks, diluted, and put back on the market. Fortunately, there were no deaths in France as the 50,000 hectoliters of adulterated Italian wine were seized before being commercialized.

Numerous substances are generated during the fermentation of fruits (ref 1). Some contribute to the organoleptic qualities of the alcoholic products obtained after distillation, while others should be present in the lowest possible amounts. Methanol falls into the latter category.

The methanol content in alcoholic products obtained through fermentation can vary significantly (ref 5). According to numerous studies, methanol is produced during fermentation through the degradation of pectins present in the initial sugar-based solution. In the case of grape fermentation, certain grape varieties lead to higher methanol content. For example, the Noah grape variety, which has been banned in France since 1935, is known for its higher methanol production.

The maximum allowable methanol content is far from negligible. In the European Union, the limit is 10 grams of methanol per liter of 100% ethanol (approximately 1.25% w/w). In the USA, the legislation is slightly stricter, allowing only 7 grams of methanol per liter of ethanol.

2 - MEASURING METHANOL IN ETHANOL

There are numerous possibilities for detecting and quantifying methanol content, and the following list is by no means exhaustive:

A purely chemical method: reduction by hydroxylamine hydrochloride in a basic medium, leading specifically to cyanhydric acid, which can be easily quantified (ref 3).

A more modern physical method: Raman spectroscopy, as methanol and ethanol have distinct spectra (ref 4).

A recent Chinese colorimetric method: a reaction with sodium nitroprusside in a basic medium, forming a colored complex that can be quantified through absorption at 481 nm (ref 7). More recently, a company has introduced a simple test that allows one to determine whether a beverage (alcohol or wine) contains more than 0.3% methanol (ref 8). No complex equipment or extensive training is needed, and the cost is not prohibitive (approximately 10 euros per test).

For electrochemistry enthusiasts, simultaneous quantification of methanol and ethanol can be performed using cyclic voltammetry on a gold electrode.

Gas chromatography is a widely favored method, particularly the one required by the European Union for the control of subsidized alcohols (ref 6). This method not only provides methanol content but also yields extensive information about other present compounds.

3 - INTRODUCTION TO THE GAS CHROMATOGRAPH

To meet the needs of our artisanal distiller, the design of the gas phase chromatograph has been greatly simplified (figure 3). The carrier gas used is ambient air, which is compressed by a miniature compressor (in fact, an aquarium air pump) capable of delivering up to 50 cm3/minute of air at a relative pressure of 0.6 bar. The column is a glass tube filled with a suitable support, operating simply within a room-temperature enclosure, eliminating the need for a heating and regulation system. The detector is a component widely used in electronic breathalyzers (MQ3 sensor), which has excellent sensitivity and comes at a very affordable price (less than 5 euros).

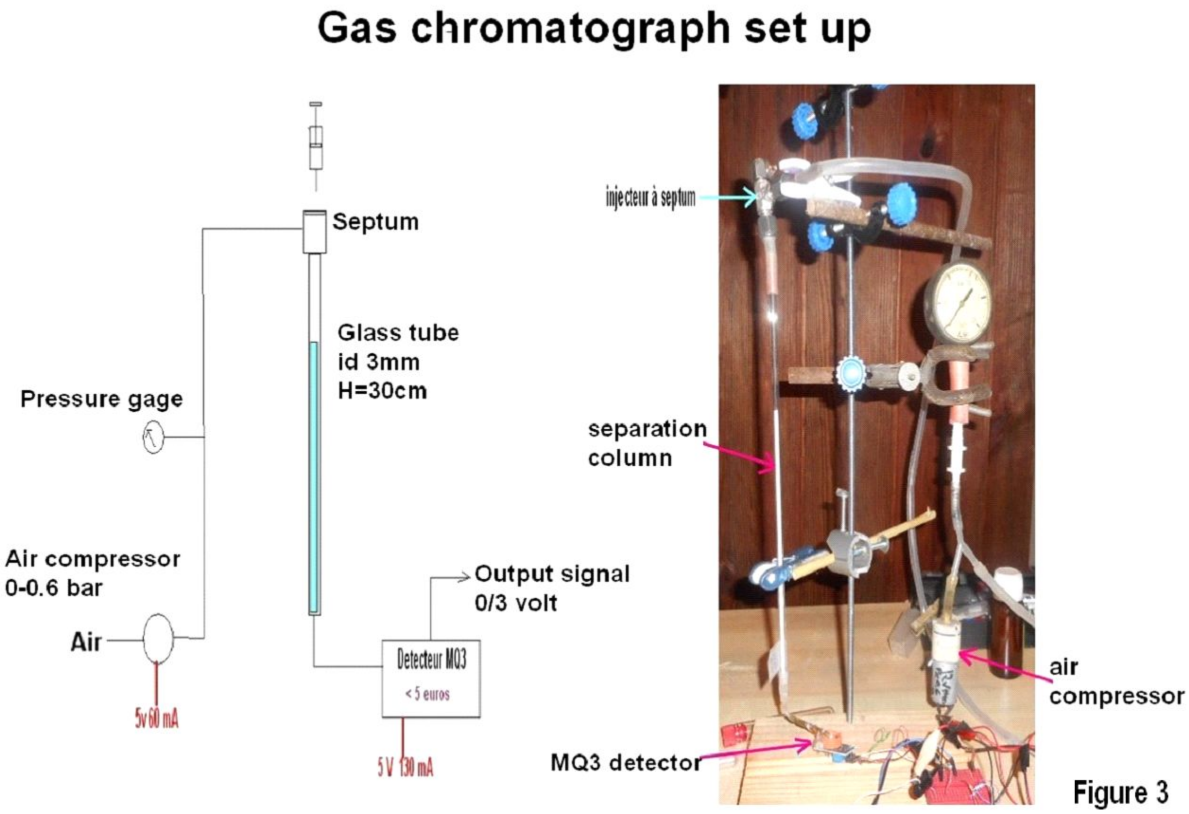


Figure 3

3-1 THE MQ3 MEASUREMENT SENSOR

This is the central part of the device. It can be purchased individually for less than 5 euros on various internet sites. It comes in two forms: either just the sensor or the sensor combined with basic electronics. The latter form is preferable for our chromatograph. The sensor should be slightly modified by removing the protective grid and attaching a small brass tube, which is in turn connected to the chromatography column's outlet, directly at the sensor.(figure 4)

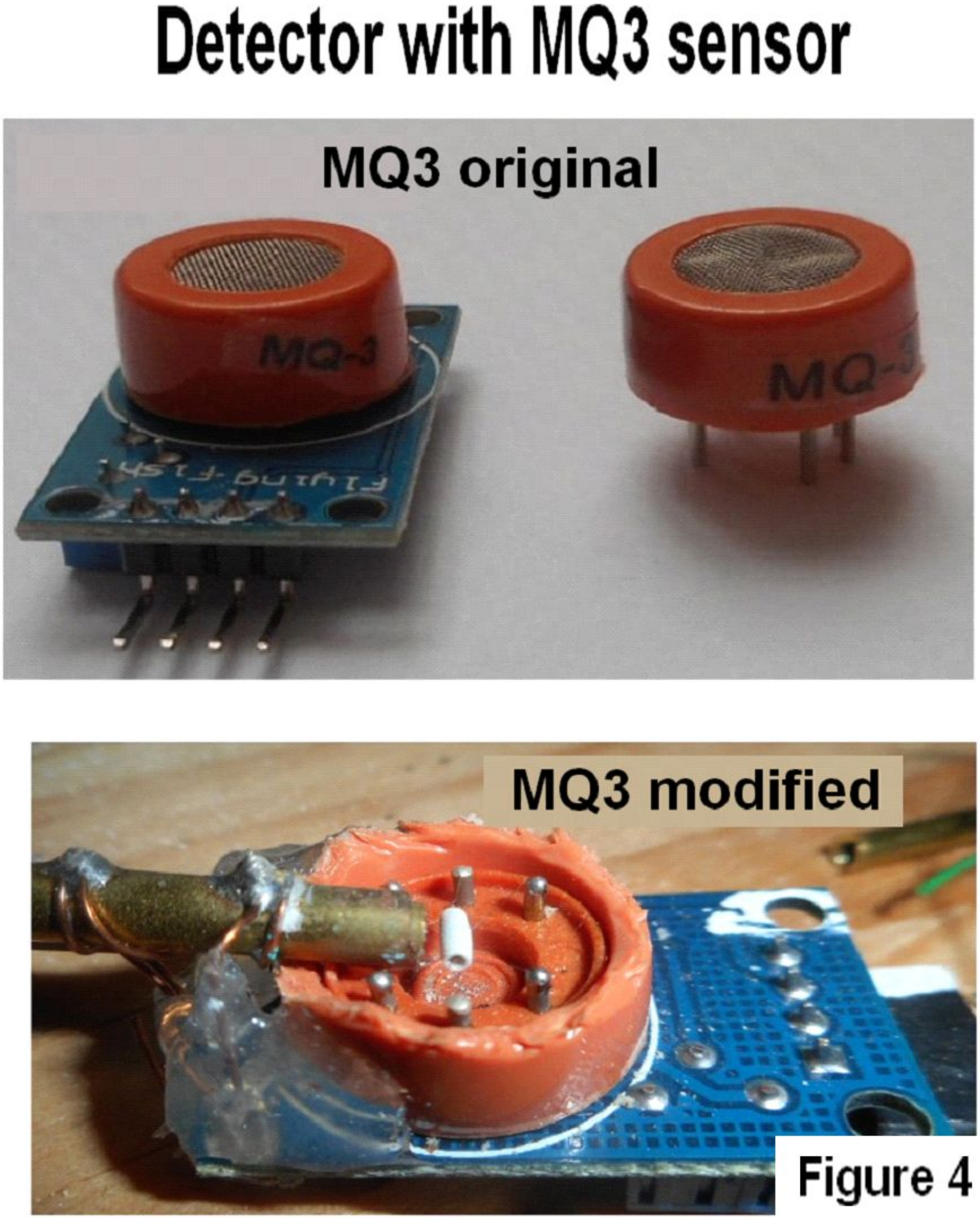


Figure 4

Here is some information about the MQ3 sensor. It is made of tin oxide doped with various compounds depending on the type of substances it is designed to detect. This element is heated by an integrated resistor. In the presence of oxidizable substances, the resistance of the element changes. By electrically connecting this element in series with a fixed resistor and powering it with a constant voltage, the sensor provides an electrical signal whose value depends on the concentration of the oxidizable substance in the immediate vicinity (figure 5). The relationship between the output voltage and the concentration is not linear. The detector's output is a function of the concentration following a relationship of the form log(output voltage) = K * log(concentration). The sensitivity of the sensor depends on the nature of the substance present. It is insensitive to the presence of water and air. To get an idea of how this type of sensor is obtained, you can refer to numerous patents, such as the one with reference 2.

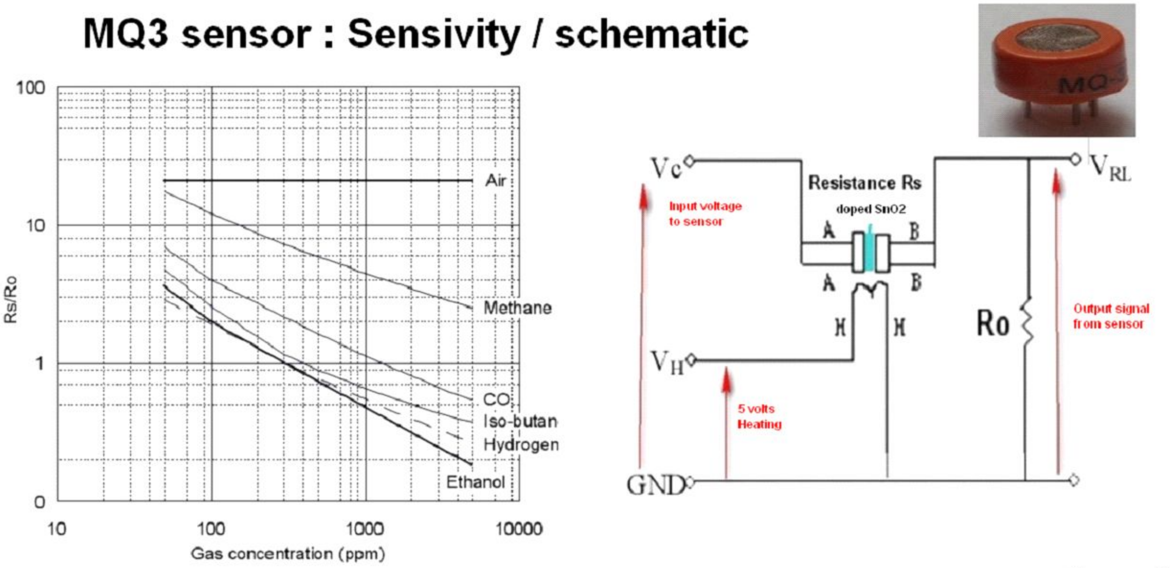

MQ3 sensor : Sensivity / schematic

Figure 5

The MQ3 sensor requires a continuous 5-volt electrical supply, with a current flow of approximately 130 mA, primarily for heating the sensor. The warm-up time is not immediate. It takes about 2 hours to reach equilibrium during the initial start-up (figure 6) . Subsequent start-ups are much quicker, requiring no more than 10 minutes. This duration is not significantly affected by the flow rate of the carrier gas.

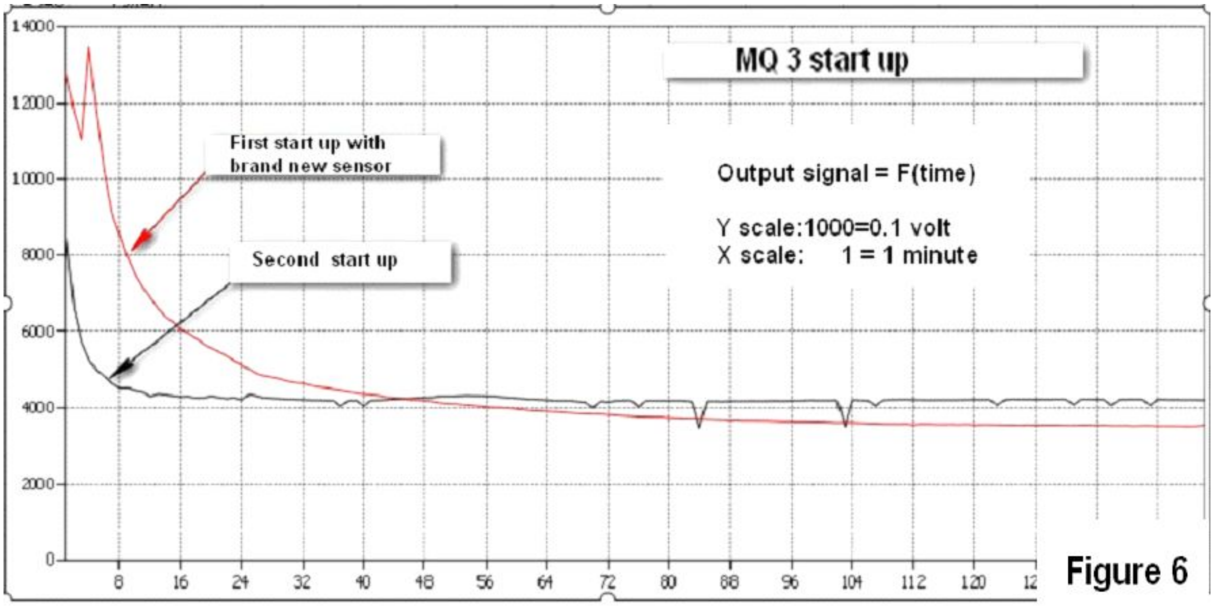


Figure 6

3-2 THE CARRIER GAS

We use air, which must be free from oxidizable substances. If desired, it can be purified by passing it through a small column filled with activated charcoal after compression. It's worth noting that carbon dioxide (CO2) can be used as a carrier gas. It is commercially available in the form of refills for homemade soda enthusiasts. In this case only a valve is needed to adjust the flow at the top of the column.

3-3 THE INJECTION SYSTEM

Figure 7

You can use septum injectors with a needle syringe or, more simply, perform injection without a septum using a pinch valve and a needleless syringe. In this case, there is no need to worry about leaks that may occur over time in the septum, not to mention the risk of needlestick injuries (figure 7) . You can inject either a liquid phase or a gaseous phase. However, in the case of a liquid phase injection, to avoid overloading the detector, the maximum volume is around 0.5 microliters, which is not very convenient. On the other hand, when injecting a gaseous phase, the volume can range from 1 to 4 cm^3, with syringes in this volume range being less expensive and easier to handle.

3-4 THE COLUMN

It consists of a glass tube (length 30 cm, inner diameter 3 mm, outer diameter 6 mm). It is filled to about 3/4 with the support material to be tested. Pressure drop depends greatly on the particle size; the finer it is, the lower the carrier gas flow rate will be. It's a good practice to measure this flow rate for each type of support material used. You don't need a sophisticated flowmeter for this; a pipette immersed in a water tank works perfectly well (figure 8).

Figure 8

The high sensitivity of the detector allows us to inject not the liquid phase to be analyzed but the vapor phase in equilibrium with it (typical an injected volume between 1 cm^3 and 5 cm^3). It is essential to purge the syringe several times between each injection to avoid any interference from the N+1 injection with the N injection, especially if the syringe is made entirely or partially of plastic.

3-5 CHROMATOGRAM VISUALIZATION

The signal provided by the MQ3 sensor is a continuous voltage ranging from 0 to 3 volts. To visualize the chromatogram, you can, of course, use a dedicated device for this task. There are many options available on the market, but they tend to be expensive. For the needs of our artisanal distiller , we opted for a lightweight and energy-efficient solution (figure 9) .

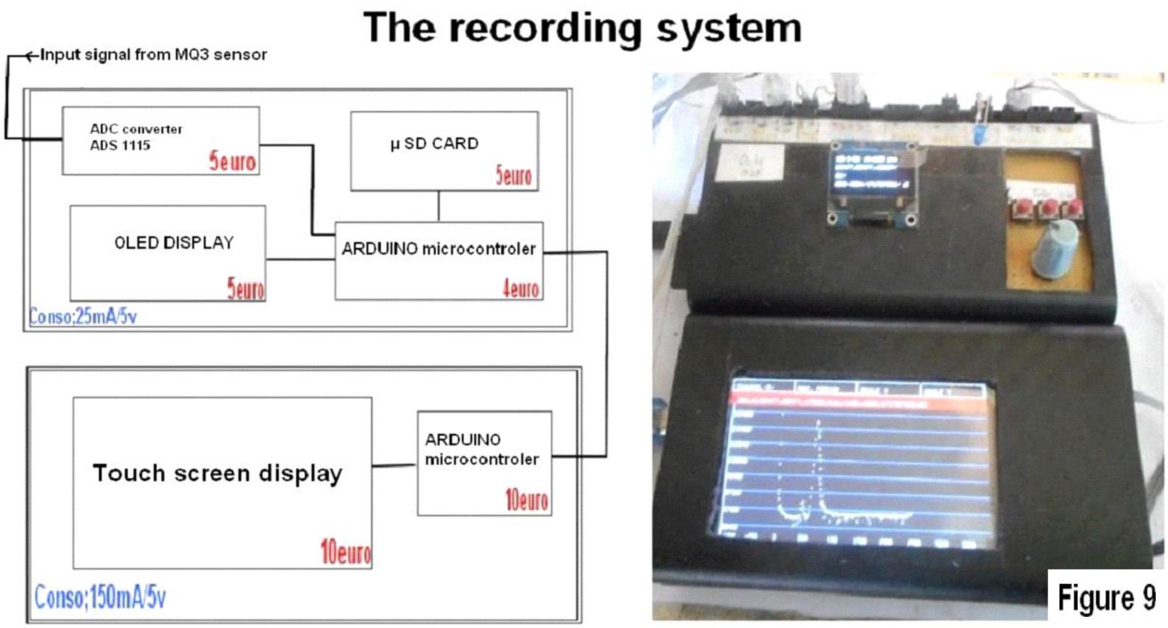


Figure 9

It consists of 2 modules: The first module, built around a microcontroller "Arduino," digitizes the signal using an ADS1115 converter, displays real-time data, stores it on a microSD card, and sends it to a second module controlling a touch screen graphical display that visualizes the chromatogram.
The entire system is particularly power-efficient, allowing battery operation (total consumption of 175 mA at 5 volts). The total cost for components purchased individually online is less than 50 euros. The chromatograms can be analyzed using graphing/spreadsheet software (Excel, Gnumeric, Xgraph, OpenOffice, etc.) by reading the files stored on the microSD card.

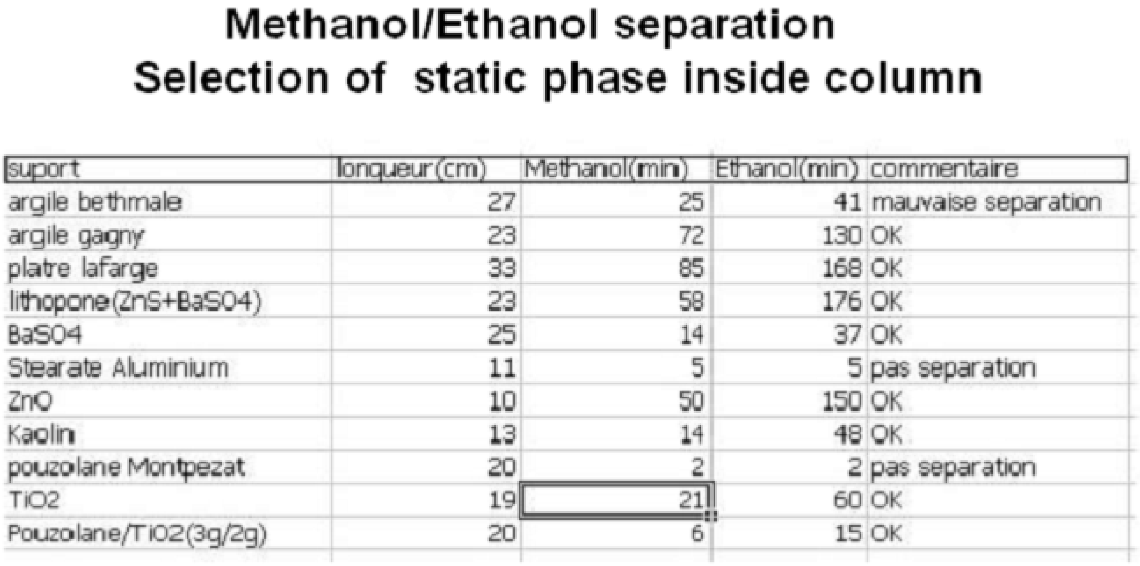
4 DEVELOPING A METHANOL/ETHANOL QUANTIFICATION METHOD

4-1 SUPPORT SELECTION

The separation of Methanol/Ethanol is relatively straightforward. Many support materials can differentiate between them. We opted for easily accessible mineral supports. The protocol involves filling the column with the test support and supplying air to achieve a relative pressure of 0.5 bar at the column head, operating at room temperature (approximately 20°C). We start with a test solution containing 66% ethanol and 34% methanol. We inject 1 cm^3 of the vapor phase in equilibrium with this solution. The table (figure 10) summarizes the results :

Length = support height in the column (in cm)
Retention time of methanol and ethanol (in minutes)

Methanol is the least adsorbed and elutes before ethanol.



Methanol/Ethanol separation
Selection of static phase inside column

suport	longueur(cm)	Methanol(min)	Ethanol(min)	commentaire
argile bethmale	27	25	41	mauvaise separation
argile gagny	23	72	130	OK
platre lafarge	33	85	168	OK
lithopone(ZnS+BaSO4)	23	58	176	OK
BaSO4	25	14	37	OK
Stearate Aluminium	11	5	5	pas separation
ZnO	10	50	150	OK
Kaolin	13	14	48	OK
pouzolane Montpezat	20	2	2	pas separation
TiO2	19	21	60	OK
Pouzolane/TiO2(3g/2g)	20	6	15	OK

Figure 10

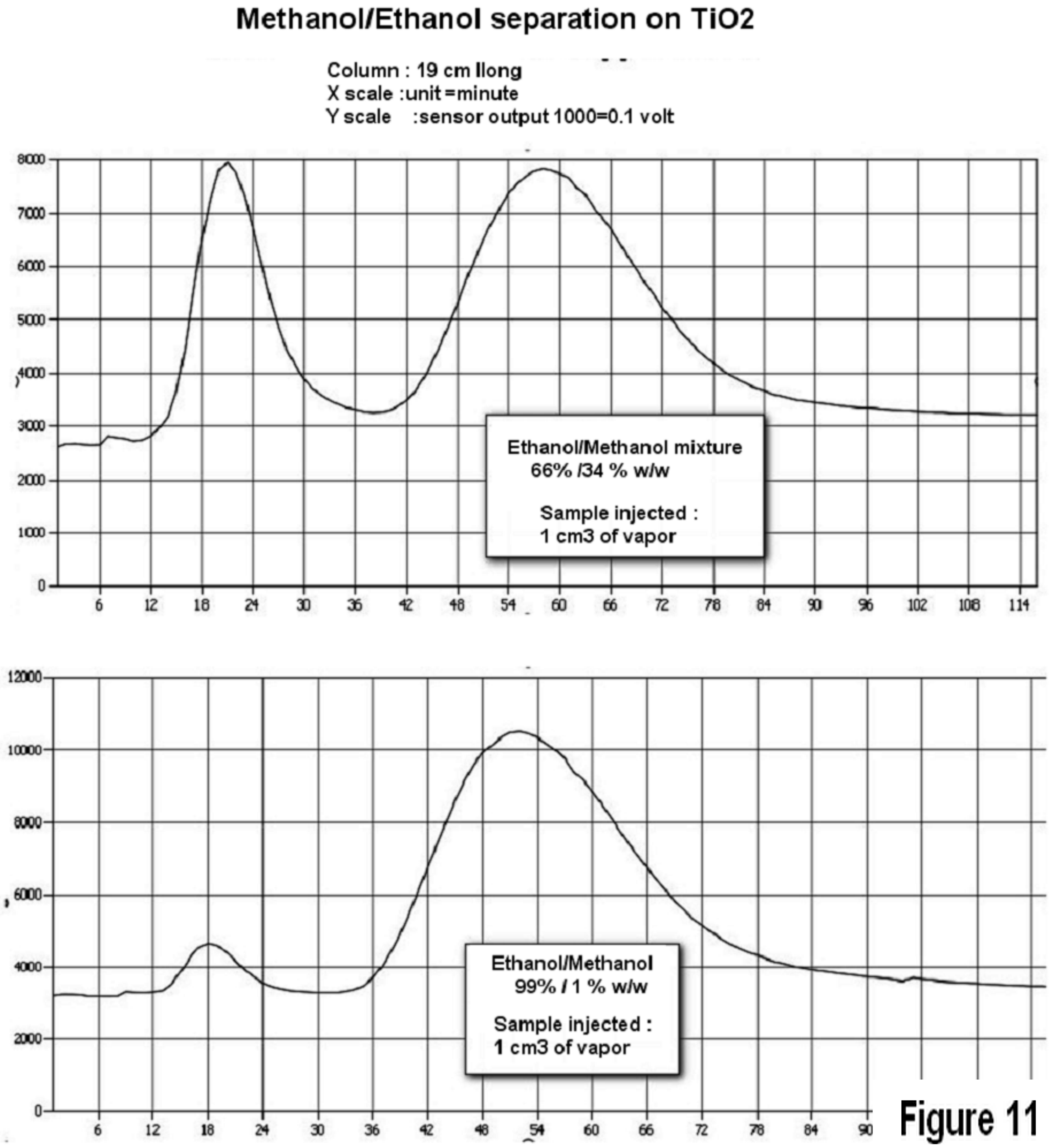


Figure 11

For the next step, we choose titanium oxide (TiO2) as the support. Above is the separation obtained for the 66% EtOH / 34% MeOH solution and the 99% EtOH / 1% MeOH solution (figure 11) .

It's worth noting that the retention times are highly dependent on the carrier gas flow rate. The test was conducted using a support where TiO2 was dispersed on pumice powder to reduce pressure drop and, consequently, increase the flow rate and reduce the analysis time (figure 19) .

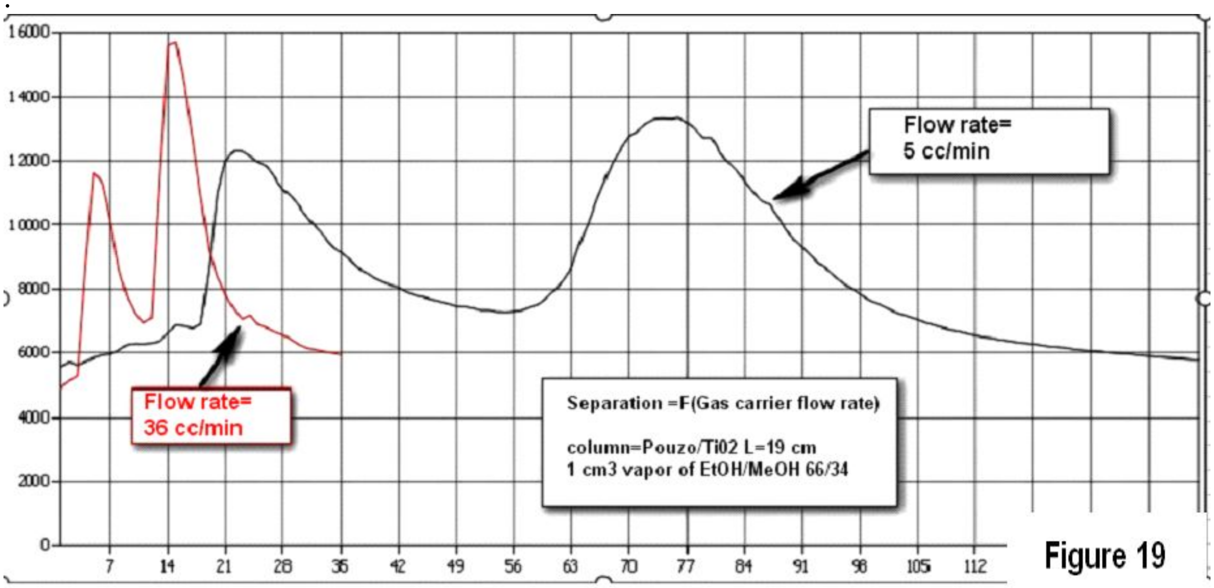


Figure 19

4-2 COMPARISON OF DIFFERENT SPIRITS

Various artisanal and commercial alcohols have been analyzed (figure 12). The methanol levels in all of them are below the maximum values allowed by European standards. It's worth noting that ethyl acetate, which is a byproduct sometimes present in certain spirits, is poorly separated under the specified conditions, leading to an overestimation of methanol content. To obtain the true value, it is advisable to reanalyze a sample previously treated with soda to decompose the acetate (sample + 3% 30% sodium hydroxide at 30°C for 15 minutes, then inject 1 cc or more of vapor).

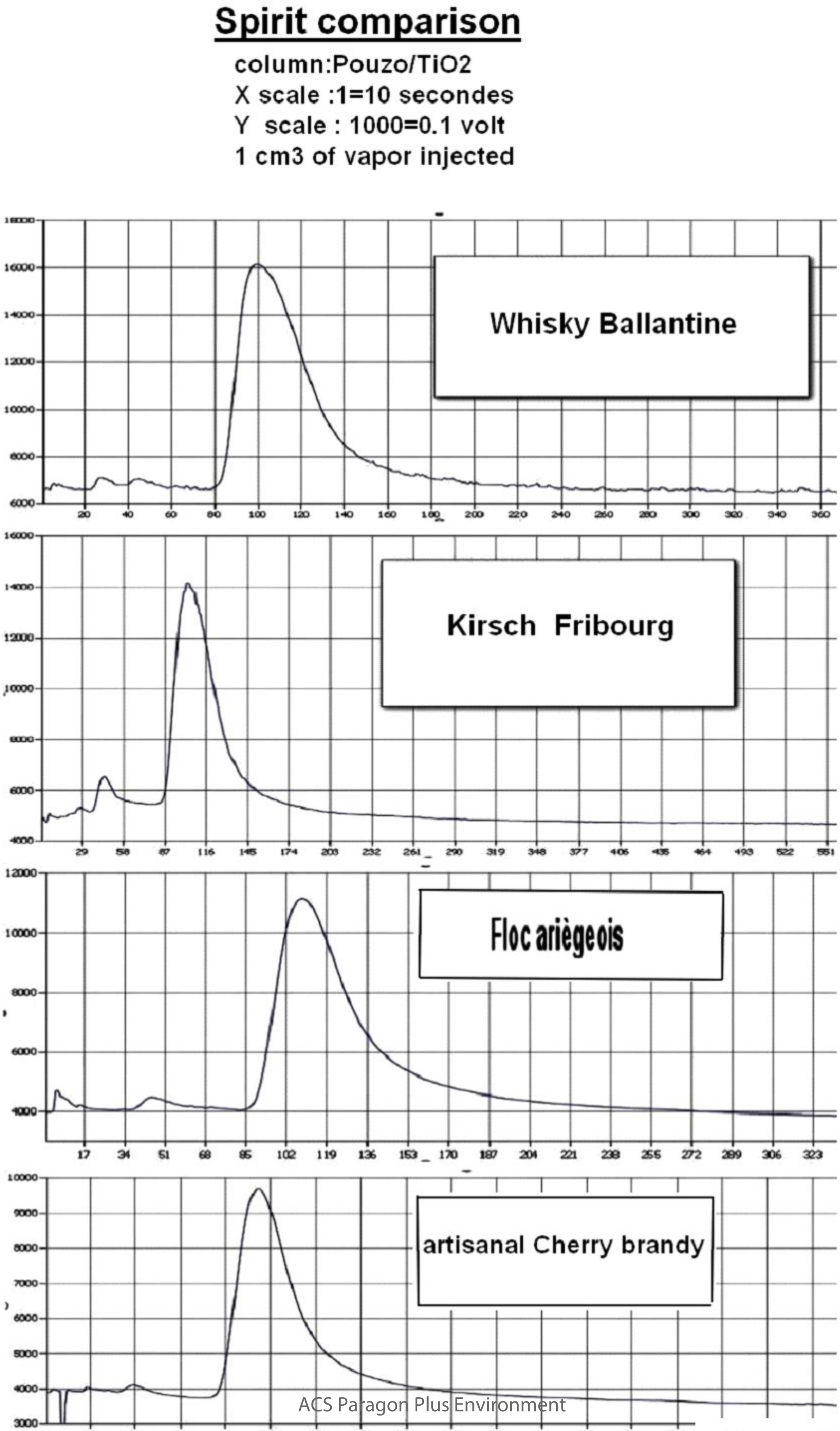

Spirit comparison
column:Pouzo/TiO2
X scale :1=10 secondes
Y scale : 1000=0.1 volt
1 cm3 of vapor injected
Whisky Ballantine
18000
16000
14000
12000
10000
8000
6000
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
Kirsch Fribourg
16000
14000
12000
10000
8000
6000
4000
29
58
87
116
145
174
203
232
261
290
319
348
377
406
435
464
493
522
551
Floc ariègeois
12000
10000
8000
6000
4000
17
34
51
68
85
102
119
136
153
170
187
204
221
238
255
272
289
306
323
artisanal Cherry brandy
10000
9000
8000
7000
6000
5000
4000
3000
23
46
69
92
115
138
161
184
207
230
253
276
299
322

Figure 12

4-3 REPLACEMENT OF THE CARRIER GAS

Carbon dioxide can be used as a carrier gas because, like air, it is not detected by the MQ3 sensor. It can be found in retail stores in small bottles containing 400 grams of CO2 for a cost of less than 10 euros. With the typically used flow rates (30 cm³/minute), the autonomy is approximately 112 hours. You will need a regulator capable of reducing the pressure in the range of 0 to 1 bar, which is also available in stores. In the case of the separation of ethanol/methanol with the used column (TiO2 support), the separation is slightly less effective than when using air as the carrier gas (figure 13) .

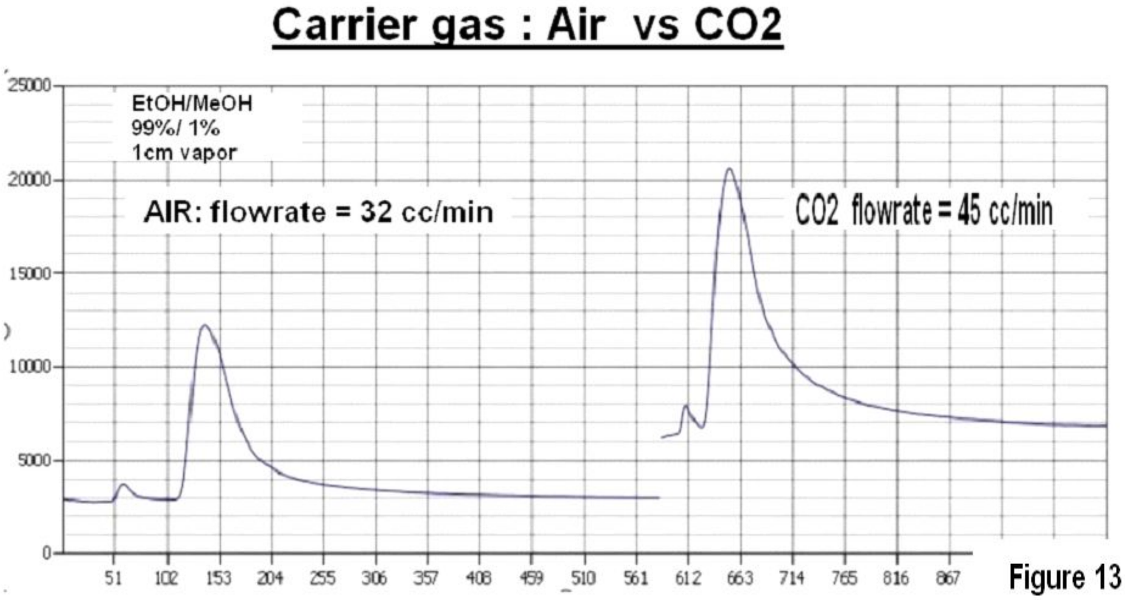


Figure 13

4-4 ETHANOL QUANTIFICATION IN FERMENTATION BROTH

The described device can be used to monitor the progress of alcoholic fermentation. To achieve the shortest response time possible, it is preferable to use a column free of any support material. Under these conditions, the system behaves as a pseudo-exponential dilutor. The height of the detector's output peak is related to the ethanol concentration in the solution. As with all tests, we inject the vapor phase in equilibrium with the liquid phase. This allows us to measure ethanol concentrations ranging from 0.01% to 10% using a calibration curve established with known standard solutions. Precision is influenced by the accuracy of the injected vapor phase volume, which may be affected by leaks in the injection system without prior knowledge. It is advisable to perform at least 2 injections to ensure accuracy. As an example, please see the results obtained by successively injecting standard solutions containing different ethanol concentrations in water, ranging from 0% to 5% (figure 14) .

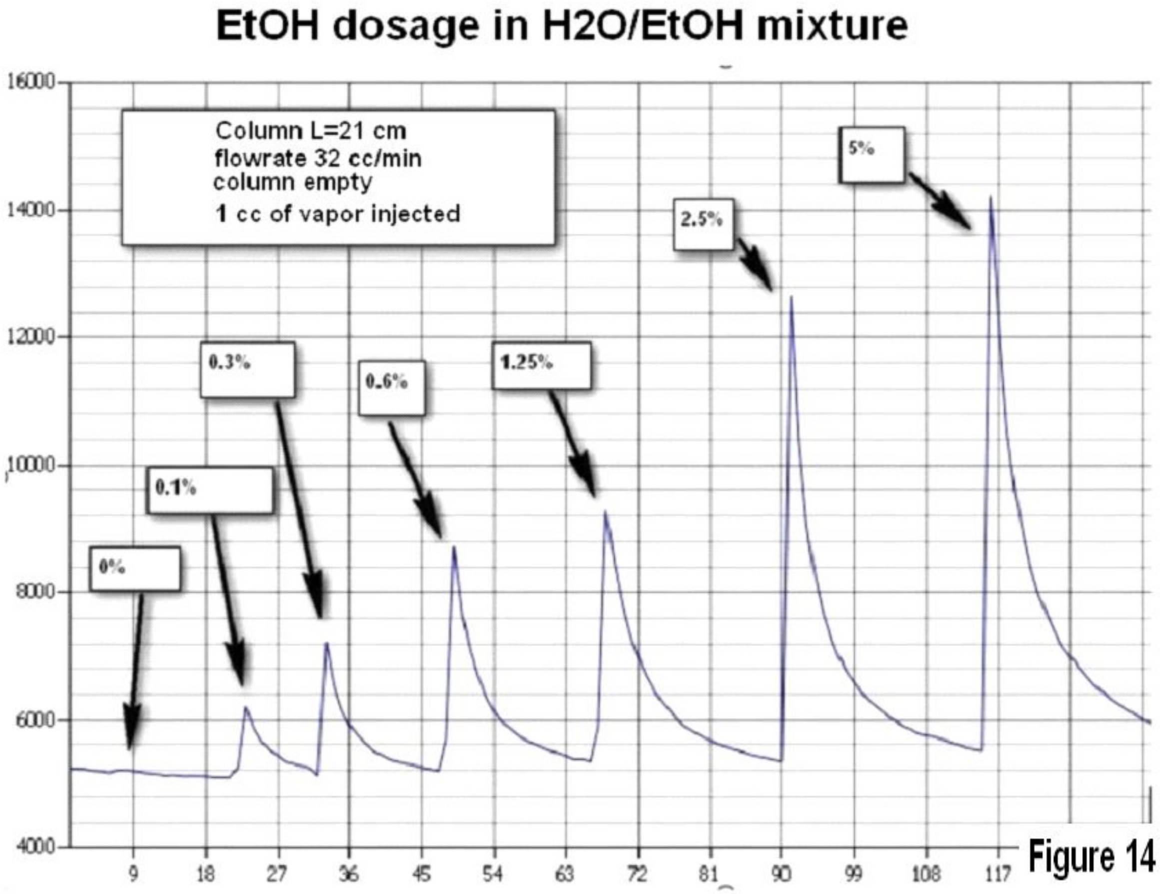


Figure 14

The relationship between the peak height and the ethanol concentration in the solution is far from linear. It is more of the form:

log (detector output voltage) = k * log (ethanol concentration)

The coefficient 'k' is only constant within a limited concentration range, as can be observed by plotting the peak height against the concentration (figure 15) .

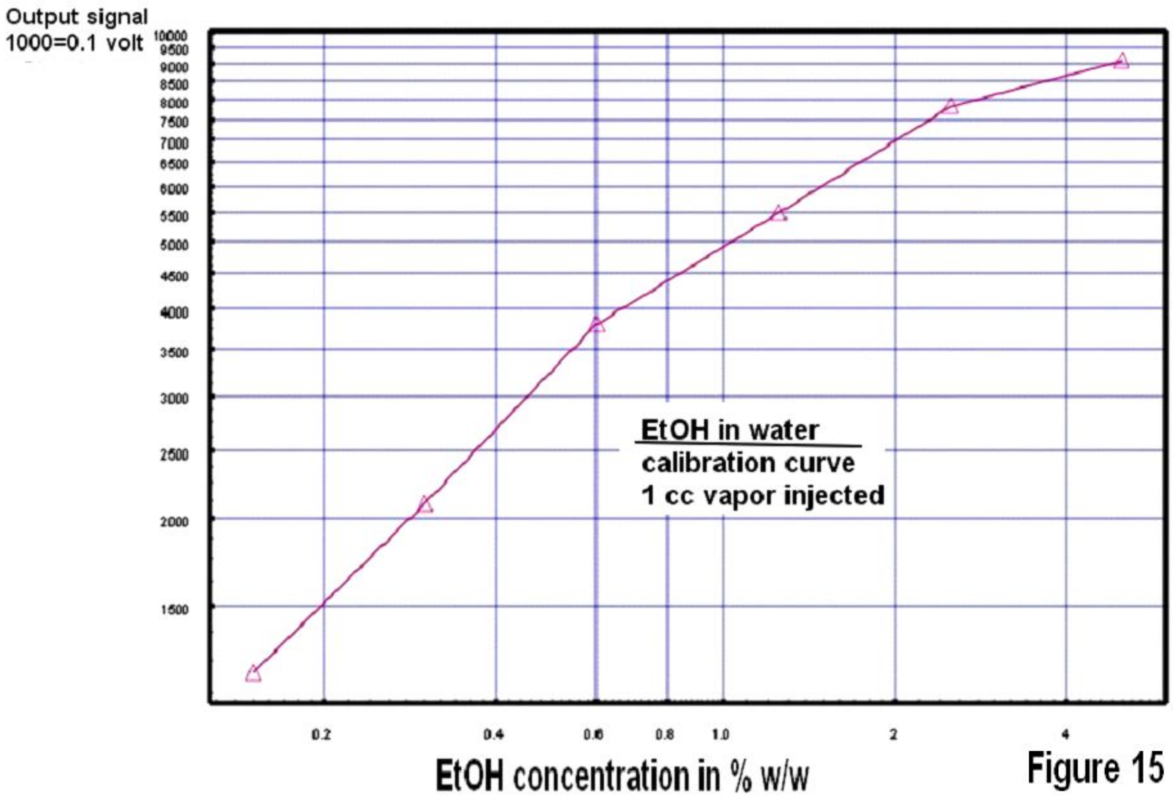


Figure 15

This measurement method is much quicker than the traditional method (figure 16), which involves distilling a sample in a miniature still, similar to the one used by our moonshiner (sampling 4 cm^3 of mash, distilling a quarter of the loaded volume, and quantifying ethanol by measuring the refractive index of the distillate). While this operation takes more time (around 20 minutes), it has the advantage of providing a sample for taste analysis.

Figure 16

4-5 SOLID-PHASE EXTRACTION

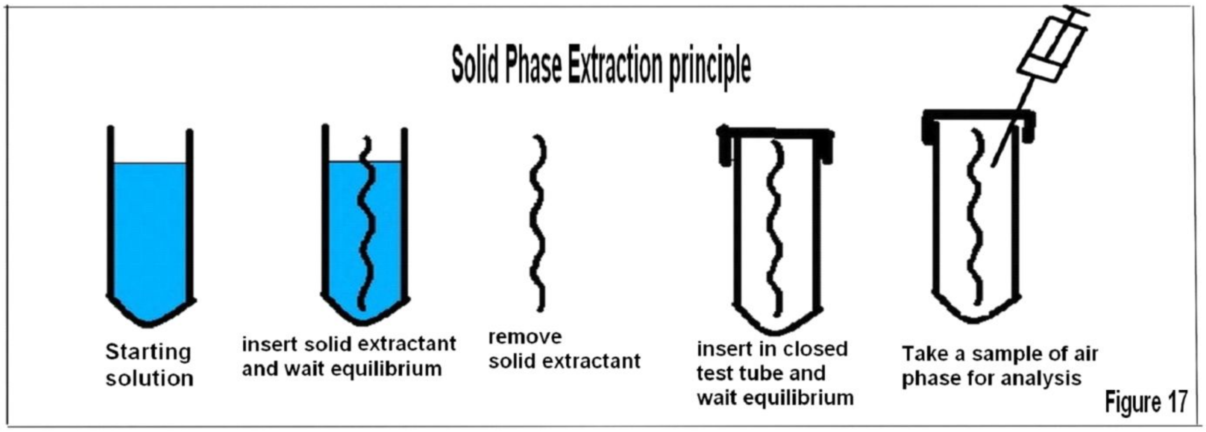


Figure 17

Solid-Phase Extraction (SPE) is an increasingly used separation technique for concentrating and analyzing compounds in complex mixtures. It involves extracting the desired compounds into a suitable solid phase and then back-extracting them into another phase (figure 17).

It can be easily implemented with our chromatograph and ethanol/water mixtures.

For this demonstration example, we start with an aqueous solution containing 18% ethanol and various esters at 0.2%, which is contained in a 10 cm³ glass test tube. We choose an agricultural plastic sheet (length = 5 cm, width = 1 cm) as the solid phase and immerse it in the solution. After 5 minutes, we remove it, quickly rinse it (in less than 10 seconds) three times with pure water by immersion, quickly dry it on blotting paper, and then place it in a 10 cm³ glass test tube filled with air. We wait for 10 minutes to establish equilibrium between the solid phase and the vapor phase. Then, we inject 2 cm³ of the vapor phase into the chromatograph.

We conducted the experiment with two different plastic films: "agricultural" polypropylene plastic and trash bag film (figure 18) . Both plastic films exhibit similar behavior and do not significantly concentrate impurities compared to ethanol. Other support materials should be explored.

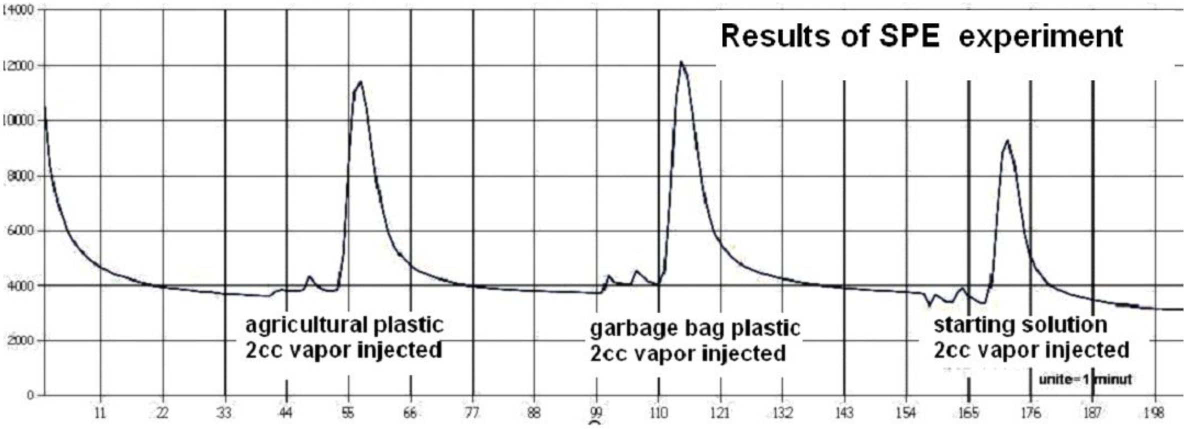


Figure 18

5 LIMITATIONS OF THE CHROMATOGRAPH

The device, as described, can only analyze products with sufficient volatility at room temperature. In practice, the boiling point of these substances at atmospheric pressure should be below 150°C . It is possible to analyze products with higher boiling points by placing the column/injector/detector in an electrically heated oven, which can reach temperatures of up to 250°C but this add complexity . The MQ3 detector, due to its design, has an internal operating temperature above 300°C at the tin oxide-based sensing element. However, the plastic coating should be removed and replaced with an electrically non-conductive support with good mechanical resistance at high temperatures (such as clay). Furthermore, the heating current needs to be reduced to maintain the detector element at its optimal operating temperature.

The other limitation of this device is its non-linearity. It expands low concentrations and compresses high concentrations, making precise measurements more challenging. However, in the estimation of trace products, this drawback becomes an advantage.

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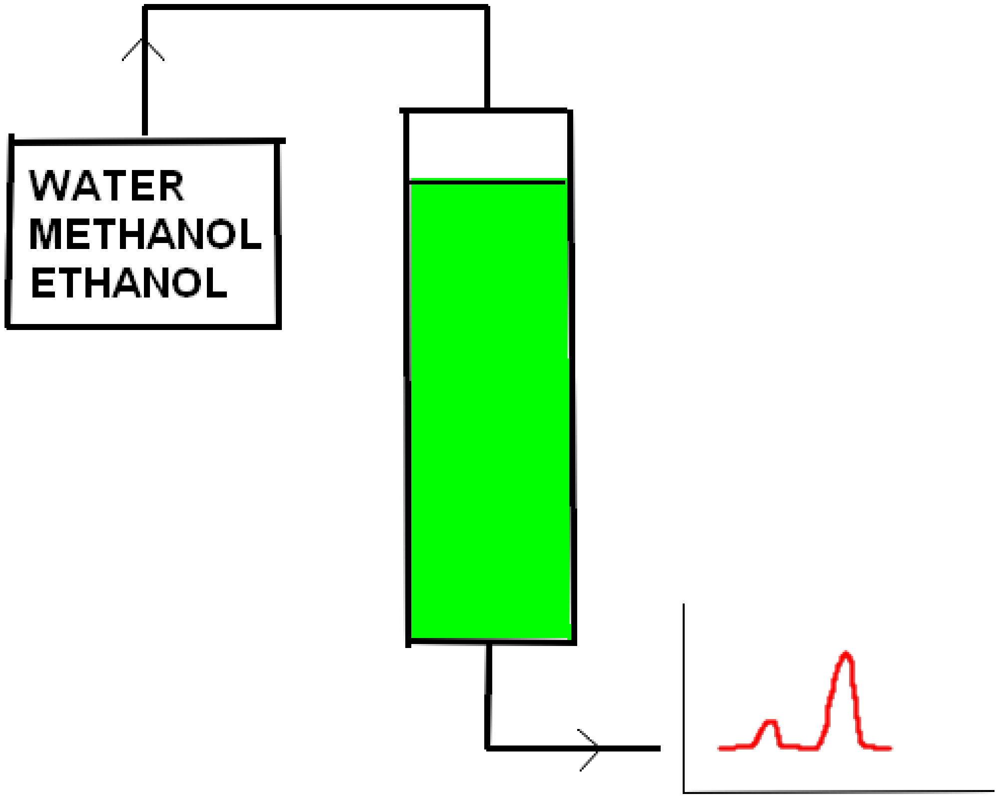
WATER
METHANOL
ETHANOL