

DOI: <http://doi.org/10.52716/jprs.v12i1.603>

## Synthesis of an Odorant Substance for Liquid Petroleum Gas (LPG) as a Substitute for Thiophene (Tetrahydrothiophene)

Muhammad Abdulkareem Swaid\*, Zeina Abdel Reda, Muhammad Allawi

Petroleum Research and Development Center, Ministry of Oil, Iraq

\*Corresponding Author E-mail: [mhnd2005m@gmail.com](mailto:mhnd2005m@gmail.com)

6<sup>th</sup> Iraq Oil and Gas Conference, 29-30/11/2021



This work is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/).

### Abstract

Tetrahydrothiophene (C<sub>4</sub>H<sub>8</sub>S) is used as an odorant for liquid gas (LPG).the Tetrahydrothiophene acts as an alarm when a leak occurs in liquid petroleum gas (LPG) bottles at a gas filling and distribution company. where it is added at a concentration of (20PPM) to the liquefied gas.

This research includes the preparation of an alternative substance to (tetrahydrothiophene C<sub>4</sub>H<sub>8</sub>S). ethanethiol (C<sub>2</sub>H<sub>5</sub>SH), that is used as an odorant for gas leaks. It was prepared in the laboratory at the Petroleum Research and Development Center through the reaction of hydrogen sulfide gas (H<sub>2</sub>S) with ethanol alcohol (C<sub>2</sub>H<sub>5</sub>OH) in the presence of a catalyst (Gama alumina) .at a temperature of (350-400 °C) using the reactor or the system that was manufactured Inside the petroleum research and development center.

The prepared substance was identified using various techniques including the (FT-IR) technique to identify the functional groups. In FTIR the thiol group (SH) clearly appeared at a frequency of (2500 cm<sup>-1</sup>) with the disappearance of the hydroxyl stretching band, which usually appears at a frequency of (3300Cm<sup>-1</sup>).

The density test for the prepared substance was also conducted using a digital density measuring device inside the laboratories of the petroleum Research and Development Center. The result was 0.8452 g/cm<sup>3</sup> at the standard temperature (15.6 °C).

The (GC-Mass) assay technique was also used, which is considered one of the most important identification tests and works to give the synthetic formula of the substance. A chart with the highest signal intensity was obtained, which is (62) that represents the molecular weight of the prepared substance ethanethiol (C<sub>2</sub>H<sub>5</sub>SH) according to what was extracted from the electronic library of the examination device.

**Keywords:** odorant substance, Ethanethiol, LPG, Tetrahydrothiophene.

## 1. Introduction

The liquid gas freshener (Tetrahydrothiophene)  $C_4H_8S$  is one of the materials that are used as an alarm, through which the consumer is warned about the presence of leakage in the containers for transporting and storing liquid gas (LPG). This substance is imported from foreign sources at a high cost of more than ten thousand A dollar per ton, and the percentage of the addition of the aromatic substance to the LPG is within (20ppm) of the amount of gas received by the gas filling company, where the amount of gas received from all the sources supplied to the gas filling company is estimated at about (4600 tons per day) Tetrahydrothiophene is prepared From the reaction of tetrahydrofuran with hydrogen sulfide gas in the presence of an alumina oxide catalyst and under specific laboratory conditions, tetrahydrofuran is obtained from the reaction of acetylene with carboxyl.

These materials and the conditions that must be provided for the production of this substance are very expensive, so the research team formed by the Petroleum Research and Development Center suggested the production of an alternative substance that does the same work as this substance and is also used globally as a scented substance for liquefied petroleum gas, a substance (ethanethiol)  $C_2H_5SH$ , and we will discuss its preparation In detail, with mentioning some of the materials that are used as a freshener for liquefied petroleum gas.

### 1.1 Liquid Petroleum Gas (LPG)

It is a mixture of hydrocarbon gases produced from refineries and oil fields, where propane and butane of its normal and branched forms constitute the largest proportion in this gas. It also contains unsaturated hydrocarbon compounds (olefins) such as propylene and butlene in small proportions. The proportions of propane and butane differ in winter and summer, where the proportion of butane increases in the summer to reduce the vapor pressure of the gas and the proportion of propane decreases, while in the winter the proportion of propane increases than the proportion of butane[1]. It can

also be defined as a flammable gas that is in the gaseous state under normal conditions, but is liquefied in order to facilitate the process of its transportation, distribution and use by raising the pressure of the gas. According to the manual of marketing specifications for petroleum products, the proportion of hydrocarbon compounds that are lighter than propane is less than 1%, and hydrocarbon compounds that are heavier than butane should not exceed 2%, and the sulfur content in LPG does not exceed (ppm150).[2]

### 1.2 Thiols

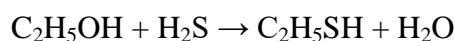
Thiols are colorless volatile liquids except for methylthiol, which is a gas, where the boiling point of thiols is lower than the boiling point of similar alcohols. For example, ethanethiol has a boiling point ( $C_2H_5SH = 35^\circ C$ ), which has an unpleasant odor and is similar to ethanol. While alcohols, including ethanol, have a higher boiling point ( $C_2H_5OH=78^\circ C$ ) than ethanethiol. This is due to the fact that the hydrogen bond between sulfur and hydrogen is much weaker than that formed between oxygen and hydrogen in alcohols, which makes the molecules in thiols less sticky while They are easily separated from each other and for the same reason, thiols are less soluble in water because they cannot form strong hydrogen bonds with water, but they dissolve in organic solvents such as ethanol, ether, chloroform and carbon tetrachloride. They are derived from hydrogen sulfide, while alcohols are compounds derived from water, which is less acidic than hydrogen sulfide. It is also noted that thiols have an unpleasant odor that is not acceptable even when When it is in very low concentrations, and for this reason, it is used in the oil industry by mixing it with gases, including propane and butane gas for alerting, as well as the means used in refrigeration to know the presence of leakage when it occurs.[3]

Sulfur is located at the bottom of oxygen in the periodic table, and the sulfur atom is characterized by being the largest in size than the oxygen atom, as well as the least electronegative, and the length of the bond (S-H) is greater than the length of the bond (O-H) as shown below.

Feature	(O-H)	(S-H)
Bond length	0.96 A	1.33 A
bond energy	463 KJ/mol	339 KJ/mol
Electronegativity	3.37	2.52

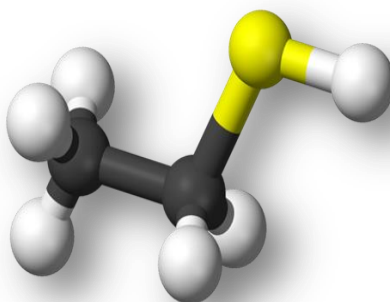
### 1.3 Ethanethiol

Ethanethiol is an organic compound with the formula C<sub>2</sub>H<sub>5</sub>SH. It is composed of an ethyl group linked to a thiol group. It is thus similar to ethanol alcohol, where an oxygen atom replaces an oxygen atom in the structure. Ethanethiol is prepared in the laboratory according to the method of preparing general thiols from the reaction of ethanol with hydrogen sulfide.



Ethanethiol has a very strong and unpleasant smell, and it is added to liquefied petroleum gas in order to detect the presence of leaks[5]. The human nose can detect the presence of this compound even if it is in small concentrations, especially since ethanethiol has high volatility due to its weak ability to form hydrogen bonds.[6]

**Properties:** Molecular formula C<sub>2</sub>H<sub>5</sub>SH (Figure 1), molar mass 62.14 g/mol, Appearance, colorless liquid ,Density 0.86 g/cm<sup>3</sup> , melting point - 148 °C ,boiling point 35 °C, Poor solubility in water. [7]



**Fig. (1) The chemical structure of Ethanethiol**

Ethanethiol is found naturally in oil and in coal tar, after its extraction,ethanethiol is converted into a hydrogenated desulfurization unit.

## **2. Experimental Works**

### **2.1 materials used**

Ethanol, hydrogen sulfide gas, iron sulfide, hydrochloric acid and catalyst  $Al_2O_3$  - $\gamma$  (Gamma Alumina).

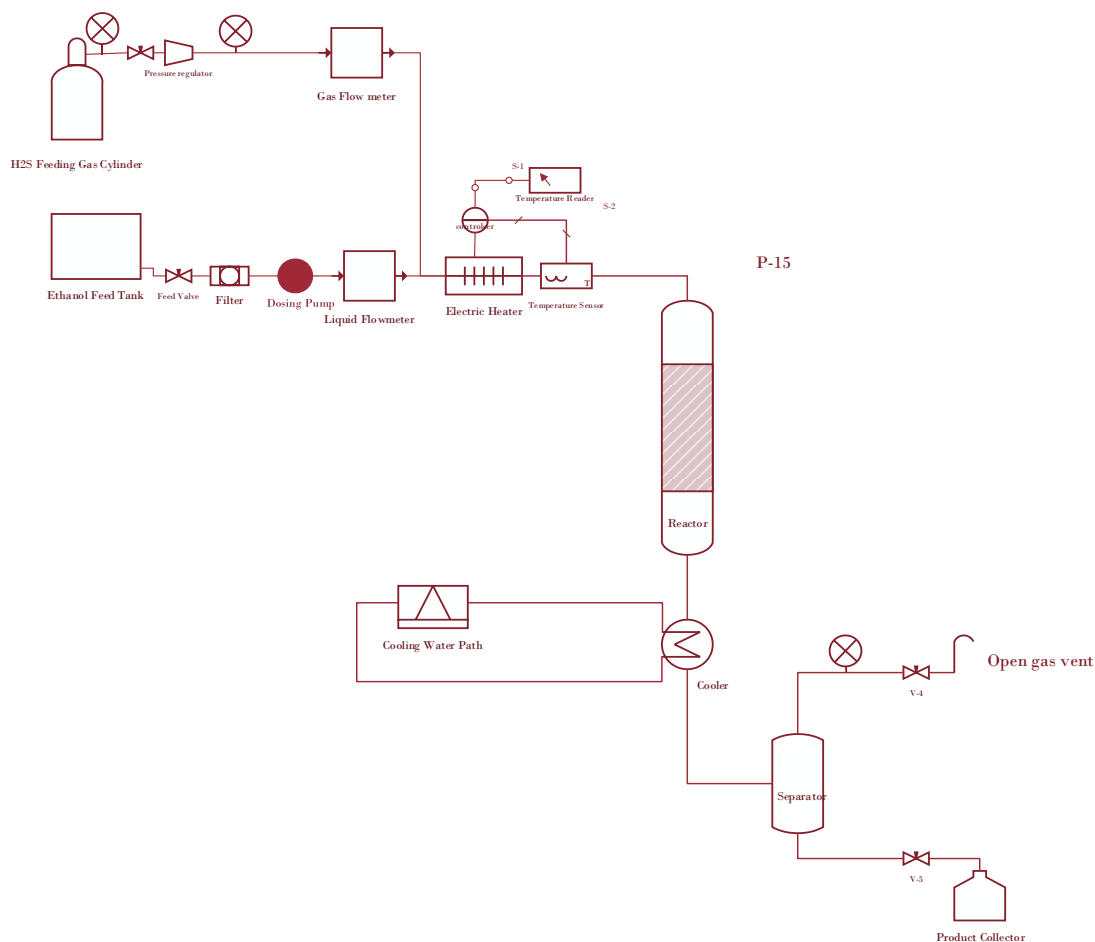
### **2.2 Method of preparation**

1- This experiment was conducted in the locally manufactured system in the Petroleum Research and Development Center shown in Scheme (1), which consists of a reactor, a thermal furnace and a cooling system connected to it, with pressure and temperature gauges, as well as a pump for entering the system's raw material liquid and another entrance for gas.

2- A gamma alumina catalyst was used

3- Hydrogen sulfide gas was used at a concentration of (1000 ppm) and pumped into the system at a pressure of 4 bar, as well as introducing ethanol into the system through a pump in the system dedicated to withdrawing the liquid and raising the temperature in the reactor that contains the catalyst gradually within a temperature (300-400) $^{\circ}C$ , noting the production, which consists of a liquid in the form of two layers (the layer of water is at the bottom and the top layer is ethanethiol due to the difference in density and polarity).[6]

4- The product was withdrawn, the water separated from the product, and a FTIR test was conducted for the produced substance, as well as a density test and a GC-mass test. It was found that the specifications of the substance produced in the Petroleum Research and Development Center match the specifications of ethanethiol in the companies producing it.



Scheme (1) Scheme of the interaction system

### 3. Results and discussion

#### 3.1 Density test

The density of ethanethiol that was prepared in the center was measured with a digital density measuring device located inside the laboratories of the Petroleum Research and Development Center shown in Figure (2) and according to the internationally approved method ASTM D-4052- 18a, where the density was measured at a temperature of 15.6°C and the result was **0, 8452 g/cm<sup>3</sup> at 25 °C** According to the international specifications of ethanethiol, its density should be **0.8315 g/cm<sup>3</sup> at 25 °C**. [8]

Through the measurement result, we note that the prepared substance conforms to the international standards for ethanethiol, with a very small difference, and it is considered normal.



**Fig. (2): Digital Density Meter**

### 3.2 FTIR Infrared Spectrophotometer Test

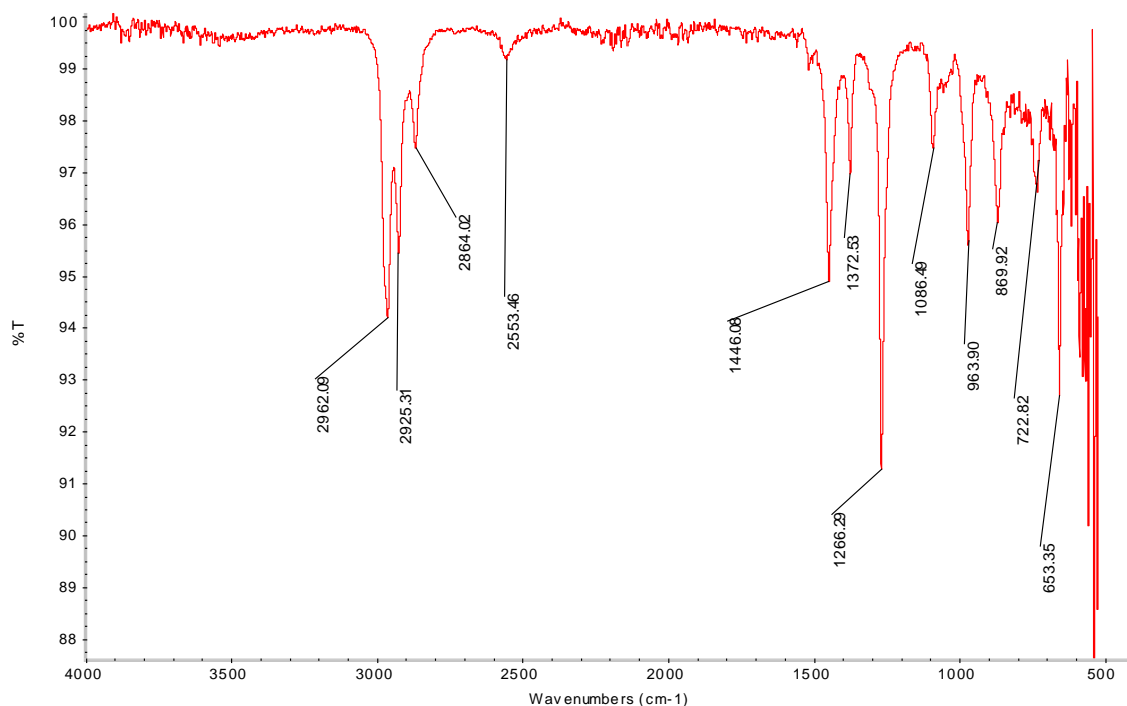
An infrared spectrophotometric test for ethanethiol, prepared by the FTIR-ATR device, located inside the laboratories of the Petroleum Research and Development Center, shown in Figure (3), was carried out according to the internationally approved test method ASTM D-3921, where a spectral chart was obtained, shown in Figure (4), and the following We explain the spectral interpretation of the chart.



**Fig. (3) FTIR-ATR device**

### 3.3 Interpretation of the infrared spectrum of the prepared ethanethiol:

The infrared spectrum of the laboratory prepared compound shown in Figure (4) showed asymmetric stretching bands for the ethylene group (CH<sub>2</sub>) at the site (2962-2925cm<sup>-1</sup>), and the spectrum showed analog stretching bands for the ethylene group (CH<sub>2</sub>) at the site (2864cm<sup>-1</sup>). , a band appeared at the site (2553 cm<sup>-1</sup>), which belongs to the thiol group (SH), as this is conclusive evidence for the formation of the compound to be prepared with the disappearance of the hydroxyl (OH) package of the primary reactant, which is ethanol, the spectrum also showed a sharp band at the site (722cm<sup>-1</sup>), which belongs to the (CS) group and another evidence for the formation of ethanethiol. The symmetric double group (CH<sub>3</sub>), while a vibration band of group (CC) appeared at the site (1266cm<sup>-1</sup>), there are several bands extending (1086-653cm<sup>-1</sup>) belonging to the group (pCH<sub>2</sub>) rocking.[9]



**Fig. (4): Infrared Spectrum of laboratory prepared ethanethiol**



### 3.4 GC – Mass test

The mass spectrometry examination was carried out in the GC mass device - located inside the gas laboratories of the Middle Refineries Company (Dora Refinery), shown in Figure (5) for ethanethiol, which was prepared in the Petroleum Research and Development Center according to the internationally approved method ASTM D 5769, where the chart shown was obtained. In Figure (6), which contains a peak with a number (62), which is higher and greater, the peak represents the molecular weight of ethanethiol, and this was confirmed by the electronic library of the GC-Mass device, where the chemical composition of the chart and peak was given, as shown in Figure (7).[10]



**Fig. (5): GC-Mass device.**

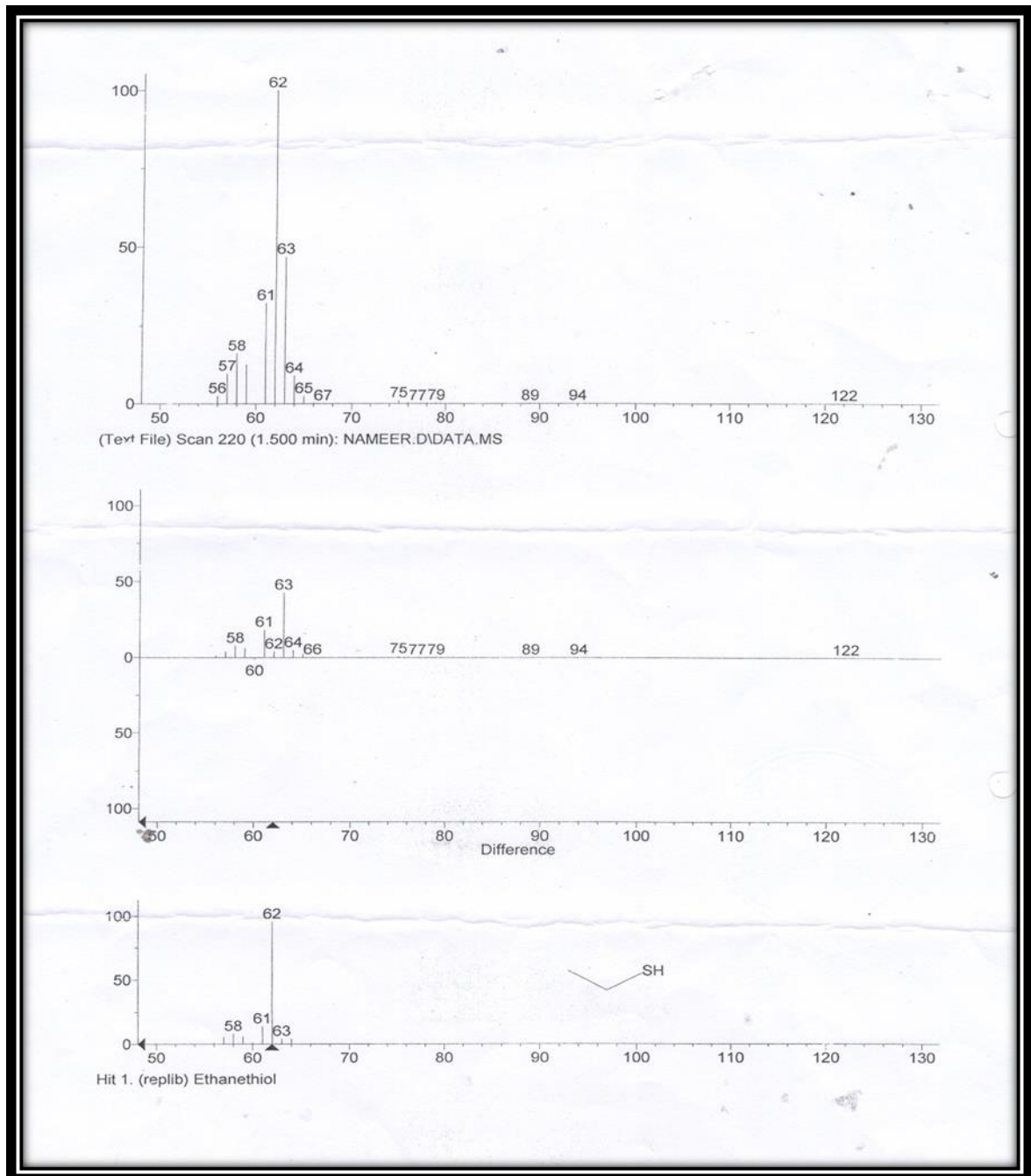
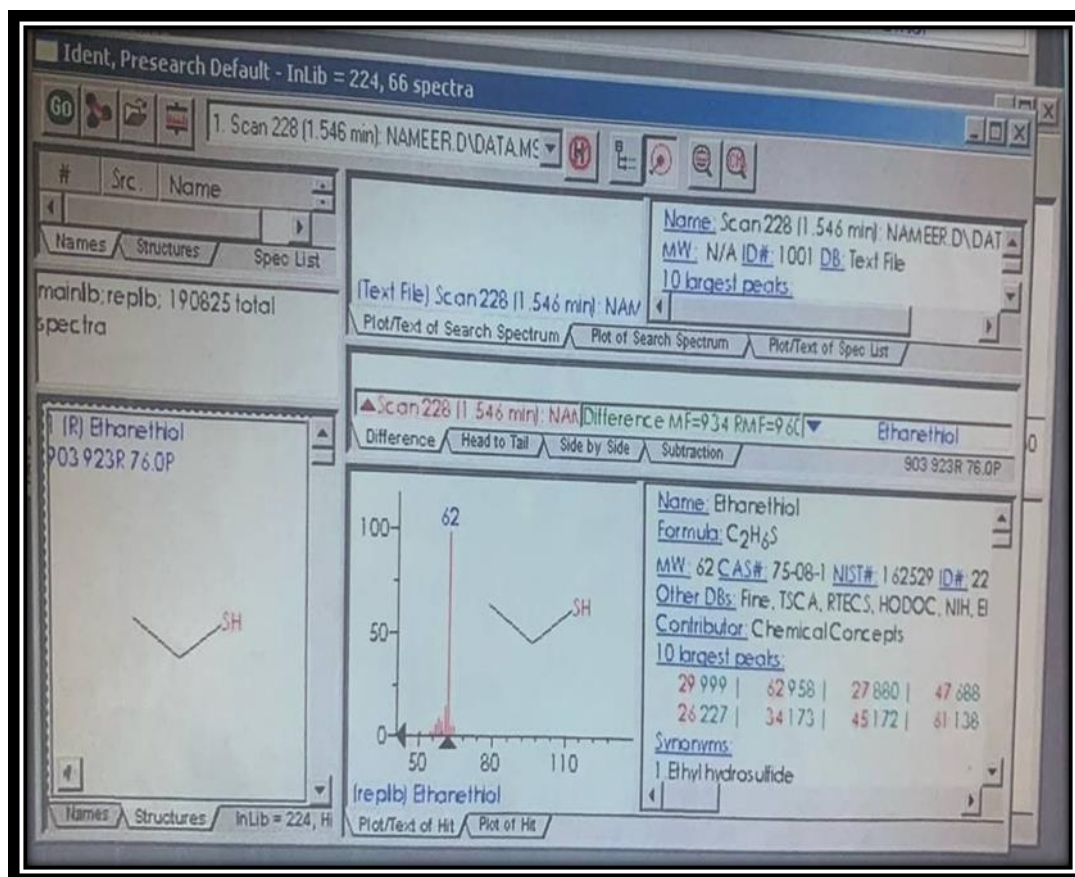


Fig. (6): Mass Spectrograph



**Fig. (7): The chemical composition extracted from the electronic library of the GC-Mass device**

#### 4. Conclusions

- 1- Raw materials used in the production of Ethanethiol are cheap from the raw materials used in the production of tetrahydrothiophene.
- 2 - Ethanethiol is widely used in countries to give off the stimulating smell of liquefied petroleum gas instead of tetrahydrothiophene, such as Canada.
- 3 - When conducting diagnostic tests for Ethanethiol manufactured in the Petroleum Research and Development Center, it gave results that match the specifications of commercial Ethanethiol.

## References

1. Madline. Refiner. Company, “Minsitry of Oil,” Baghdad.
2. “Ministry of Oil,” vol. 22, p. 1998, 2019
3. O’Neil, M.J. (ed.). The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals. 13th Edition, Whitehouse Station, NJ: Merck and Co., Inc., 2001.
4. “The Chemistry of Thiol Group, Part 1 (Patai’s Chemistry of Functional Groups) book.
5. Mirrington, R. N.; Feutrill, G. I., "[Orcinol Monomethyl Ether](#)". *Org. Synth.; Coll. Vol.* 6: 859, (1988).
6. Hasenberg, Daniel M., and Mitchell D. Refvik. "Process and catalyst for synthesis of mercaptans and sulfides from alcohols." U.S. Patent No. 7,399,893. 15 Jul. 2008.
7. C. Science, “properties Safety,” pp. 1–10, 2010.
8. Lide, D.R., G.W.A. Milne (eds.). Handbook of Data on Organic Compounds. Volume I. 3rd ed. CRC Press, Inc. Boca Raton ,FL. 1994., p. V3: 2660
9. W. Simon, “Spectrometric identification of organic compounds,” *Microchemical Journal*, vol. 7, no. 3. p. 388, 1963, doi: 10.1016/0026-265x(63)90068-7.
10. “Ethanethiol | C<sub>2</sub>H<sub>5</sub>SH - PubChem.” [Online]. Available: <https://pubchem.ncbi.nlm.nih.gov/compound/Ethanethiol>.