

APPROVAL

The thesis titled "**INDUSTRIAL SAFETY AND ENERGY MANAGEMENT RELATED TO LPG BOTTLING PLANTS**" submitted by **Mohammed Ainul Islam, ID No: 14MET011P and Session: 2014-2015** has been accepted as satisfactory in partial fulfillment of the requirements for the degree of Master of Science (M.Sc.) in Energy Technology on **18th May 2023**.

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The author hereby acknowledges and declares that the thesis was studied and written entirely by himself and that the work has never been submitted for any other degree or professional qualification. To the best of his knowledge, the contained material was not authored or published by anybody except for the appropriate references mentioned.

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LIST OF PUBICATIONS

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ABSTRACT

Liquefied Petroleum Gas (LPG) is regarded as a safe and cost-effective alternative to natural pipelined gas. It is a flammable gaseous hydrocarbon compound formed mostly of propane (C_3H_8), butane (C_4H_{10}), and isobutene (C_4H_8), or even a combination of these, and liquefied at ambient temperature and moderate pressures, produced as a byproduct of crude oil or natural gas processing. It has a high heating value and reduces emissions by 75% (CO), 10% (CO_2), 40% (NO_2), 85% (ozone-depleting gases), and 85% (unburned hydrocarbons). There are many LPG bottling plants in Bangladesh. LPG leakage occurs while unscrewing screws or filling a cylinder from the carousel or in the pipeline. LPG accidents occurred generally from flash fire, VCE, pool fire, fire ball, BLEVE, Leak, etc. In such circumstances, worker safety is essential, and energy security is required for energy consumption. The main objective of this study was to investigate the hazards of LPG and its effect on bottling plant worker's safety and the environment due to leakages of LPG.

We have analysed threat zone of the LPG bottling plant by using ALOHA software (point/area modelling). It was found that the threat zone increases with increasing LPG release and decreasing wind velocity (for the same amount of LPG release). On the other hand, propane is more hazardous than butane and isobutene. In cases of toxicity, the explosion tendency of LP gas varies in the order of butane>isobutene>propane.

From the analysis of radionuclides impact on LPG, it is found that due to the release of LP gas during bottling, the ^{222}Rn concentration in the airborne was increased (from 0.024 to 1.243pCi/l) in various parts of the LPG bottling plant. It depends on the volume of the room and the quantity of LP gas released. Workers of the LPG bottling plant and the people of the nearby area take in these radioactive particles through inhalation.

The average ($n=5$) values of radium equivalent activity(R_{eq}), representative level index (I_γ), external hazard (H_{ex}), internal hazard (H_{in}), Absorbed dose(AD), Annual effective dose (AED) and Excess life time cancer risk are $40.34Bqkg^{-1}$, 0.292, 0.108, 0.1316, 19.12 nGy.h^{-1} , 0.023 mSv.y^{-1} and $8.21\times 10^{-5}Sv^{-1}$ respectively.

The hazard indexes (HI) from the LPG are less than one, indicating no health risk to human health for the heavy metals (As, Co, Cr, Fe, Mn and Zn from the LPG) daily inhaled.

সারসংক্ষেপ

তরলীকৃত পেট্রোলিয়াম গ্যাস (এলপিগিজ) প্রাকৃতিক পাইপযুক্ত গ্যাসের নিরাপদ এবং সশ্রয়ী বিকল্প হিসাবে বিবেচিত হয়। এটি একটি দাহ্য বায়বীয় হাইড্রোকার্বন যৌগ যা বেশিরভাগ প্রোপেন (C_3H_8), বিউটেন (C_4H_{10}), আইসোবিউটিন (C_4H_{10}), বা এমনকি এইগুলির সংমিশ্রণে গঠিত এবং পরিবেষ্টিত তাপমাত্রা এবং মাঝারি চাপে তরল করা হয়, যা অপরিশোধিত তেলের এবং প্রাকৃতিক গ্যাস প্রক্রিয়াকরণের উপজাত হিসাবে উৎপাদিত হয়। এটির উচ্চ মান রয়েছে এবং এটির নিগমন 75% (CO), 10% (CO_2), 40% (NO_2), 85% (ওজোন-ক্ষয়কারী গ্যাস) এবং 85% (অপূর্ণ হাইড্রোকার্বন) হ্রাস করে। বাংলাদেশে অনেক বোতলজাত এলপিগিজ প্লান্ট রয়েছে। ক্ষু খুলতে বা ক্যারোজেল থেকে সিলিন্ডার ভর্তি করার সময় বা পাইপলাইনে এলপিগিজ লিকেজ হয়। এলপিগিজ দুর্ঘটনা সাধারণত ফ্লাশ ফায়ার, ভিসিই, পুল ফায়ার, ফায়ার বল, ব্লেভ, লিক ইত্যাদির কারণে ঘটে। এই ধরনের পরিস্থিতিতে, প্লান্ট এর কর্মীদের জন্য নিরাপত্তা অপরিহার্য, এবং শক্তি খরচের জন্য শক্তি নিরাপত্তা প্রয়োজন। এই অধ্যয়নের মূল উদ্দেশ্য ছিল এলপিগিজের প্রক্রিয়াজাতকরণ সমস্যা এবং এলপিগিজ লিক হওয়ার কারণে বোতলজাত প্ল্যান্টের শ্রমিকদের নিরাপত্তা এবং পরিবেশের উপর এর প্রভাব তদন্ত করা।

পয়েন্ট/এরিয়া মডেলিং দ্বারা ALOHA সফটওয়্যার ব্যবহার করে বিভিন্ন পরিমাণ এলপিগিজ রিলিজ সহ এলপিগিজ বোতলজাত প্ল্যান্টের বিপদজনক অঞ্চল বিশ্লেষণ করা হয়েছে। এখানে আমরা লক্ষ্য করেছি যে এলপিগিজ রিলিজের পরিমাণ বাড়ার সাথে এবং বায়ুর গতিবেগ হ্রাসের সাথে (একই পরিমাণ এলপিগিজ রিলিজের জন্য) বিপদজনক অঞ্চল বাড়ছে। অন্যদিকে প্রোপেন বিউটেন এবং আইসোবিউটেন চেয়ে বেশি বিপদজনক। বিষাক্ততার ক্ষেত্রে, এলপি গ্যাসের বিস্তারনের প্রবণতা বিউটেন > আইসোবিউটিন > প্রোপেন এর ক্রম অনুসারে পরিবর্তিত হয়।

তরলীকৃত পেট্রোলিয়াম গ্যাসে রেডিওনিউক্লাইডের প্রভাবের বিশ্লেষণ থেকে, এটি পাওয়া যায় যে বোতলজাত করার সময় এলপি গ্যাস রিলিজ হওয়ার কারণে, এলপিগিজ বোতলজাত প্ল্যান্টের বিভিন্ন অংশে বায়ুবাহিত ^{222}Rn ঘনত্ব ($0.024-1.243 pCi/l$) বৃদ্ধি পেয়েছে। এটি ঘরের আয়তন এবং বোতলজাত করার সময় নির্গত এলপি গ্যাসের পরিমাণের উপর নির্ভর করে। এলপিগিজ বোতলজাত প্ল্যান্টের কর্মীরা এবং আশেপাশের এলাকার মানুষ শ্বাস-প্রশ্বাসের মাধ্যমে এই তেজস্ক্রিয় কণা গ্রহণ করে। রেডিয়াম সমতুল্য কার্যকলাপের গড় ($n=5$) মান (Req), প্রতিনিধি স্তরের সূচক (I_γ), বাহ্যিক বিপদ (H_{ex}), অভ্যন্তরীণ বিপদ (H_{in}), শোষিত ডোজ (AD), বার্ষিক কার্যকর ডোজ (AED) এবং অতিরিক্ত লাইফ টাইম ক্যান্সারের ঝুঁকি হল ক্রমান্বয়ে $40.34 Bqkg^{-1}$, 0.292 , 0.108 , 0.1316 , $19.12 nGy.h^{-1}$, $0.023 mSv.y^{-1}$ এবং $8.21 \times 10^{-5} Sv^{-1}$ ।

এলপিগিজের বিপদ সূচক (HI) একের কম, যা এই ভারী ধাতু (As , Co , Cr , Fe , Mn এবং Zn) দৈনিক শ্বাস-প্রশ্বাসের জন্য মানব স্বাস্থ্যের জন্য কোন স্বাস্থ্য ঝুঁকি নির্দেশ করে না।

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LIST OF ABBREVIATIONS

Abbreviation	Term
AAS	Atomic Absorption Spectrometry
AERE	Atomic Energy Research Establishment
GIS	Geographic Information System
HPGe	High Purity Germanium
IAEA	International Atomic Energy Agency
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
INAA	Instrumental Neutron Activation Analysis
NAA	Neutron Activation Analysis
NDNAA	Non-Destructive Neutron Activation Analysis
PIXE	Proton Induced X-Ray Emission
SRM	Standard Reference Material
SL	Lake Sediments
TS	Top Soil
TXRF	Total Reflection X-Ray Fluorescence
WHO	World Health Organization
XRF	X-ray Fluorescence

CHAPTER I

INTRODUCTION

1.1 HISTORY OF LPG

It is often assumed that gaseous fuels were developed during the difficult days of World War II when gasoline shortages were prevalent. Importantly, and maybe unexpectedly, LPG was initially utilized as a vehicle fuel long before the conflict began.

In the United States, a propane-butane combination was first mentioned in 1910. Walter O. Smelling, an American scientist studying the qualities of gasoline at the time, separated the gaseous and liquid fractions, discovering an abundance of propane. In 1912, two years later, he began his first household installation of propane in 1913. He was the first to patent industrial-scale propane manufacturing. Later that year, Frank Phillips, the founder of the Conoco Phillips oil corporation, purchased the patent. Nevertheless, LPG usage did not increase significantly. LPG was first used in practical applications in 1918, when it was used to power brazing lights and metal-cutting flame throwers. Yet commercial manufacturing did not commence until the 1920s. In 1922, LPG sales in the United States reached 223 thousand gallons, and within three years, the volume has increased to four million gallons. LPG was initially utilized as a motor fuel (in a truck) in 1928, and the first LPG freezers were built. In 1929, gasoline sold up to 10 million gallons in the United States. LPG was quickly making inroads. It was used for boiling water and cooking at the 1932 Olympics in Los Angeles. The propane-butane industry was expanding annually, and in 1934 it produced and sold a total of 56 million gallons of LPG. The prominence of airships that routinely sail between Europe and the United States increased demand for liquefied petroleum gas in the following year.

The known as Blau gas (developed by Herman Blau) was used to power the airships in the Zeppelin series, which were then at the height of technological development, which was remarkably similar to butane - one of LPG's constituents. Since gaseous fuel did not significantly alter the total weight of a zeppelin in the same way that liquid fuel would, it was really rather helpful for airships. Regrettably, when the Hindenburg, the world's biggest airship, was destroyed in a fire in 1937, killing 36 people, the zeppelin period came to an end [1].

Fortunately, the LPG period did not come to an end with it. On the contrary, it flourished because of the high quantity of gas bottles left on airfields where airships worked. For example, 6,000 of them became obsolete in Rio de Janeiro alone, prompting entrepreneur Ernesto Igel to purchase them and promote gas as an effective cooking fuel. This is how the Brazilian corporation Ultragaz, subsequently known as Ultragas, was founded. The firm had three distribution vans and 166 clients by 1939. Eleven years later, in 1950, there were over 70,000 clients, and now Ultragas is one of the world's largest LPG operators. [1].

As World War II ended and industrial production resumed, LPG sales in the United States surpassed 1 billion gallons. At the time, about 62% of all American houses had LPG installations. The first liquefied gas tanker was produced and put into operation in 1947. In 1950, the Transit Authority of Chicago, a public transportation provider in Chicago, bought 1000 buses powered by LPG, while 270 cabs in Milwaukee were also converted in that year. LPG sales topped 7 billion gallons in 1958, and Chevrolet developed four new LPG-powered engines for commercial cars in 1965. The first international shipping agreements were reached in the 1950s. Yet, the volume of exported LPG was still modest in the 1960s, with less than 1 million tons sent outside of the United States. For the next 20 years, exports increased to 17 million tons, reaching 48 million tons in 2000. [1]

LPG started in Europe for the first time during the mid-1930s, as it was imported from the USA and introduced in France. It must have been bottled and originated on the East Coast. In a plant near Venice, the Italian company Liguigas began filling bottles with LPG in 1938. In the following years, the beginning of World War II, however, halted further development on the Old Continent. [1].

1.2 SOURCE OF LPG

LPG is created via the processes of extracting natural gas and refining petroleum. In order to process LPG, the gas must first be separated from its petroleum source and collected. LPG is obtained from mixtures of hydrocarbons through the processing of crude oil or natural gas. The initial phase in both activities is finishing the drilling of petroleum wells. A gas trap, where it is separated into crude oil and "associate" gas (LPG and natural gas), is used to extract the gas/oil mixture from the well. The heavier crude oil is fed into an oil processing tank from the bottom of the trap where it settles.

Figure 1.1 illustrates some of the procedures used to refine crude oil, including catalyst cracking and crude distillation. Figure 1.2 displays the LPG generation process from "associate gas."

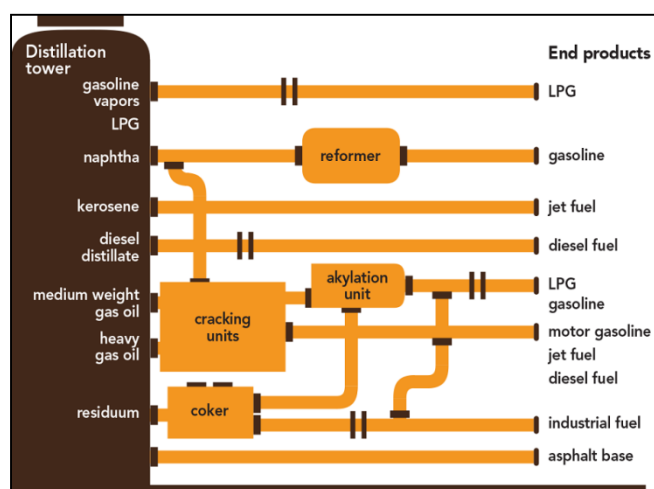


Figure 1.1 Shows a Basic Refinery's Schematic. [2].

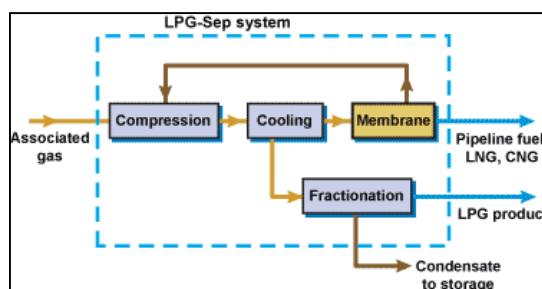


Figure 1.2: LPG is Refined from Associated Gas [2]

1.3 PHYSICAL PROPERTIES OF LPG

Table 1.1 compares the physicochemical characteristics of several LPG gases. The pressure in an LPG (propane) container is temperature dependent. At temperatures ranging from -43°C to 70°C , the pressure inside the LPG (propane) container is 0 bar to 24.8 bar. Pressure increases when the LPG canister is exposed to intense heat. The LPG valve that releases pressure allows gas to escape if the pressure rises over a safe level, keeping the pressure in the LPG cylinder within reasonable bounds. The typical pressure setting for an LPG reliever valve is 2585 kPa, or 25 bar [2].

The variations in pressure corresponding to temperature are shown in the Table 1.2. LPG is a liquid in a cylinder with a pressure-sensitive region at the top which it converts into LPG vapor. The liquid LPG is at the bottom of the container, while the vapor pressure of the LPG gas is maintained at the top, as indicated in the following figure

(Figure 1.3). The typical LPG cylinder fill level is 80%, which is 80% liquid and 20% vapor. The proportion of liquid LPG reduces as the gas is used [2].

Table 1.1: Physical Properties of Different LPG Gases [2]

LPG Gases	Units	Propane	Butane	Isobutane
Chemical Formula		C ₃ H ₈	C ₄ H ₁₀	C ₄ H ₁₀
Energy Content	MJ/m ³	95.8	111.4	110.4
Energy Content	MJ/kg	49.58	47.39	45.59
Energy Content	MJ/L	25.3	27.5	25.0
Boiling Temperature	°C	-42	-0.4	-11.75
Vapor Pressure at 21 °C	kpa	858.7	215.1	310.9
Flame Temperature	W/Air	1967	1970	1975
Expansion	m ³ /L	0.54	0.405	0.402
Gaseous Volume	m ³ /kg	356	51	3.6
Relative density (water=1)		0.51	0.58	0.60
Relative density (air=1)		1.53	2.00	2.07
Specific Volume	L/kg	1.96	1.724	1.669
Specific weight	Kg/L	0.51	0.58	0.60
Gas Specific Gravity at 25°C		1.55	2.07	2.06
Gas density 15°C	Kg/m ³	1.899	2.544	2.533

Table 1.2 Correlation Between LPG (Propane) Cylinder Pressure and Temperature [2]

Temp		Pressure		
°C	°F	kPa	PSIG	Bar
70	158	2482	360	24.8
60	140	2013	292	20.1
54	130	1794	257	17.9
43	110	1358	197	13.6
38	100	1186	172	11.9
32	90	1027	149	10.3
27	80	883	128	8.8
16	60	637	92	6.4
-1	30	356	51	3.6
-18	0	152	24	1.5
-29	-20	74	11	0.7
-43	-45	0	0	0

The cylinder vapor pressure are changes with the change of temperature of the LPG cylinder. Which is different for different gases. Vapor pressure increases rapidly with

change of temperature and maximum rises for 100% propane. Which is shown in Figure 1.4.

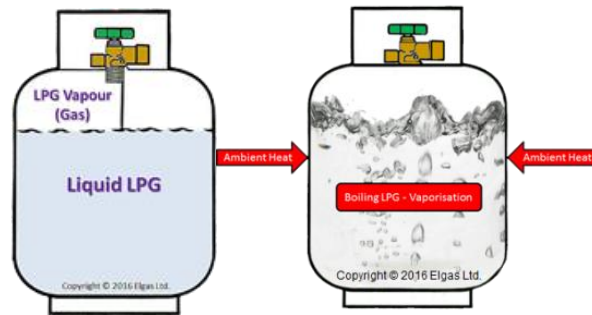


Figure1.3: State the LPG Inside the Cylinder [2]

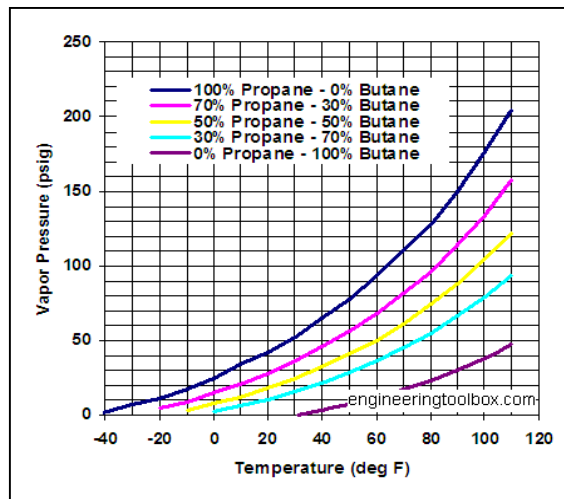


Figure 1.4: Vapor Pressure of Different LPG Corresponding Temperature in the Cylinder [2]

1.4 ADVANTAGE OF LPG

LPG is a fuel that is both affordable and environmentally beneficial. It is a 100-octane fuel that is lead-free, has a lower sulfur level than regular gasoline, and doesn't need any additional additives to perform better. In the event of a leak, the only component, ethyl-mercaptan, produces an odor that can be readily detected. As may be seen in the numbers below, burning it releases far less carbon dioxide, carbon monoxide, and water vapor than gasoline vapors. Carbon monoxide emissions are reduced by 75%, carbon dioxide emissions are reduced by 10%, incomplete combustion hydrocarbons are reduced by 85%, nitrogen oxides are reduced by 40%, and ozone-depleting gases are reduced by 85%. In addition, when compared to diesel engines, it emits at least 90% less soot [3].

1.5 USES OF LPG

Although LPG is primarily used as a fuel in kitchens and ovens, it is also used in other settings, including industry, agriculture, and homes. The GPL permits the use of homogeneous heating equipment of any type, controlling the purity of the process, the modulation of the flame, concentration, control, and temperature stability for applications in the steel industry, foundry, pulp and paper, glass, ceramics, food, beverage, plastics, cement, asphalt, metallurgy, automobile, shipbuilding, textile, chemical industry, pharmaceutical industry, and cosmetic industry, as well as hundreds of other applications that make LPG an energetically high per unit fuel [3].

1.6 DEMAND FOR LPG IN BANGALDESH

For overpopulated developing countries like Bangladesh, where there are many more consumers than there are fossil resources, the availability of fuel and energy sources has always been a concern. The nation is depended largely on stored natural gas in all regions [4]. The country's energy consumption is gradually growing. Natural gas is the country's primary energy source, although supply is insufficient to meet demand. The annual gas consumption is 1TCF, and gas demand is expected to exceed 58.2TCF until the year 2050. The country is now experiencing a gas crisis. The pipeline supply is not accessible across the country. This difficulty may be solved by using liquefied petroleum gas (LPG). Because of its extremely clean burning, low cost, and ease of transportation, LPG demand is skyrocketing. Currently, Bangladesh's LPG consumption is around 100,000MT per year. LPG facilities in Chittagong, Sylhet, and Kailashtila provide around 15–20% of the current demand, with private imports covering the remaining 80% [5]. Over 95% of LPG consumption is imported from nations such as Singapore, Malaysia, Saudi Arabia, Abu Dhabi, and Kuwait. To address a market need, private enterprises collaborate with them. The government is promoting the use of LPG through favorable policies and incentives.

However, the LPG business is predicted to quadruple by 2021 and reach 2.5 million tons, with many industry personnel in the pipeline and modest product variety disparities. When gas sources become scarce, CNG cars will be switched to LPG fuel or autogas [6].

LPG is used for home and commercial purposes in the modern world. In addition, it serves the industrial, chemical, refining, and price-sensitive needs for associated gas. Natural gas is now neither exported nor imported. Because of this, domestic

consumption growth has increased at a rate of 7% annually over the past few decades, following domestic output growth. Figure. 1.5 illustrates how much of Bangladesh's

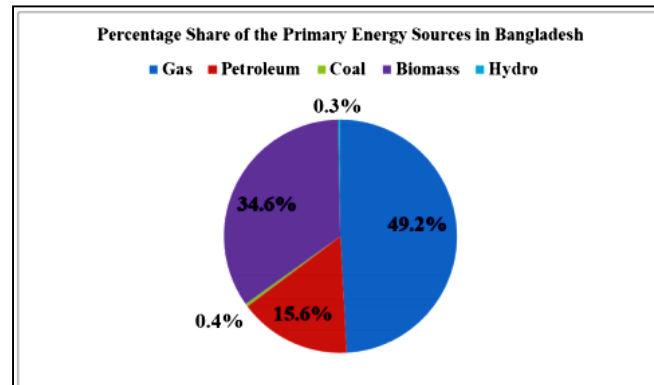


Figure 1.5: Primary Energy Sources in Bangladesh [5]

principal energy sources are covered by petroleum gas: 15.6%. LPG is used for home applications for approximately 81% of its total volume. A Well-planned road map is designed to enable LPG operators to provide 70% of residential cooking fuel used in 2025 [7].

1.7 LPG SUPPLY CHAIN

Figure. 1.6 depicts the supply chain diagram from LPG manufacturing to distribution. It is clear that transportation plays a significant role in LPG handling. LPG is delivered via a variety of modes of transportation throughout the world, but it is typically done so by trains and roadways. LPG is now carried via lengthy pipes, which are more convenient and safer. Due to a lack of LPG production capacity in Bangladesh, refinery companies imported LPG through large ships to fulfill supply and demand.

More than 95% of the nation's LPG demand is met by private imports from Kuwait, Singapore, Malaysia, Saudi Arabia, Abu Dhabi, and the state-owned oil firm of Saudi Arabia, Saudi Aramco. There are more than 18 LPG terminals in Bangladesh as of 2018. Because huge ships cannot access certain rivers from the deep sea, this is known as the draft problem. The cost of distribution rises as a result. Because the shore lacks suitable import facilities, interior travel is necessary and expensive. Several LPG companies have built about 15 satellite filling stations (Bashundhara LP Gas and Omera Petroleum each have three LPG satellites) to promote and keep up the LPG cylinder chain across the country.

LPG transportation by road is more expensive than LPG transportation by river in tiny

LPG boats. The dispersion procedure for LPG in Bangladesh is shown in Figure 1.7. The seaport is a crucial component of LPG imports since LPG is transported on cargo

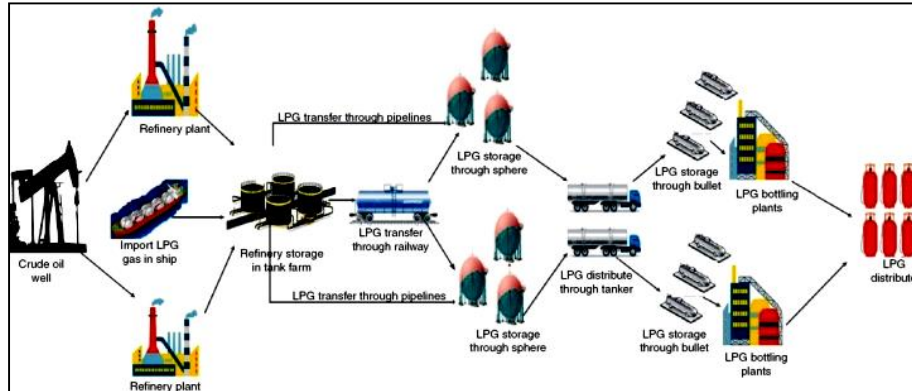


Figure 1.6: Supply Chain Diagram of LPG Production to Distribution [8]

ships. However, Saudi Aramco contract rates and government regulations pose significant obstacles to Bangladesh's LPG supply. When supplying LPG to Bangladesh, the following issue may arise [7].

- i. LPG is hazardous. Special jetties are required for LPG imports.
- ii. Jetties can't receive more than 10000MT of gas.
- iii. LPG prices are changing year by year and month by month.
- iv. Terminal located near ports that have draft restriction.

A significant challenge is figuring out how to develop and grow LPG supply networks safely and profitably. There are three crucial factors: 1) Establishing cylinder depots and a coordinated network of cylinder transportation networks to service communities from urban to semi-urban to the farthest places are the locations of physical facilities and logistics. 2) Decentralizing filling entails dispersing smaller storage and filling facilities throughout different regions. 3) A system will be in place for a specialized or franchisee-based distribution channel to ensure that each LPG marketer cylinder is swiftly returned to it for inspection, maintenance, scrapping (if necessary), and refilling. Price cuts and promotions will also be fully advantageous to consumers. Brand preferences and loyalty might be taken into consideration [9].

Channel for Safe Distribution: A safe distribution path guarantees 1) Compliance with safety and maintenance requirements at the specific LPG bottling plant. 2) LPG transport vehicle safety precautions are routinely inspected (truck & booth tanker). 3) Utilization of personal protection equipment (PPE) by channel partners when loading,

unloading, and delivering LPG cylinders to clients. 4) In distributor, dealer, and end-user locations, there is an adequate supply of fire safety equipment. There are also visible safety signs and safe environment procedures. [9].

Distribution Channel Challenges: Even if there are still many issues, the following are some crucial areas to take into account: 1) Cross-filling is currently posing a danger to the LPG industry. Many illegal traders decant from one cylinder to another using illegal methods. Customers consequently receive underweight, hazardous, and fake refill gas. Unwelcome gas leaks and explosions may also be caused by these conditions. A small satellite plant owner has occasionally been observed filling cylinders from various brands (source: press sources). This is problematic for the creation of a suitable supply chain. The market may finally hold up, but stakeholder confidence will decline, legal market participants' investments in cylinders will stall or stop, public safety and welfare will suffer, and cross-fillers' share of the LPG market will increase. It is great if the government enacts regulations that limit this kind of person's actions. Then, throughout the duration of the industry's development, the government must continue to successfully enforce this. 2) Strong wholesaler, dealer, and retail control on end-user pricing: Due to the fact that LPG companies only work with large distributors, the channel frequently caps prices for a variety of factors, including company expenses, consumer preferences, supply shortages, and more. 3) Inadequate infrastructure, which slows product distribution to end customers via the channel. 4) Transportation costs, a lack of educated labor, a suitable location to store LPG cylinders, and other factors all contribute negatively. 5) Unseen bureaucratic complexities and other variables [9].

Need for Government Support: As the LPG market grows, the amount of activity, the number of competitors, and the complexity of the market necessitate governmental intervention in the areas of 1) adequate regulatory enforcement, which must take place throughout the nation. 2) Government-funded initiatives to increase public knowledge of LPG. 3) Include LPG in the national mix of energies [9].

As the market grows, there will be less demand for government-owned LPG (supplied by LPGL under BPC), as a strong private LPG enterprise made up of knowledgeable, experienced, larger-scale businesses and a strong federal LPG connection can help the government through an agreed-upon degree of self-regulation and other types of public-private collaboration.

Assistance from Private LPG Businesses: Personal LPG Marketers must abide by all

applicable laws, regulations, and norms. They must strengthen this market's development through their investments and efforts. Through safety awareness efforts,

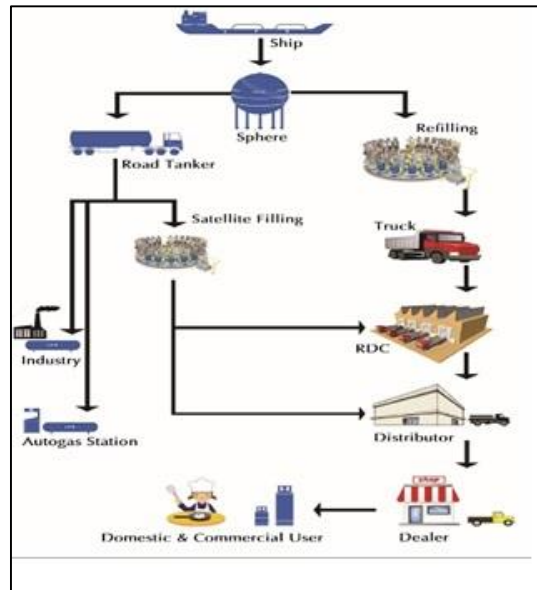


Figure 1.7: Chain Diagram of LPG Distribution in Bangladesh [7]

they should inform current and potential consumers about how to use LPG safely. Workshops, lectures, rural activation programs, the delivery of safety awareness leaflets, etc. are all part of these efforts. Additionally, companies should arrange sessions to enlighten the distribution channel about regulatory obligations, industry standards, and corporate responsibility. This will help boost channel partners' understanding of the importance of safety. To inform the public about the advantageous and safe use of LPG, technical specialists from LPG firms will go to all parts of the nation, from urban areas to the most rural. The decision to continue, suspend, or decrease current investment in the industry will ultimately be made by LPG marketers, their partners, investors, and terminals [9].

1.8 RADIATION

The movement of waves or particles through a material medium is the emission or transfer of energy as radiation. Depending on the energy of the released particles, it can be classified as ionizing or non-ionizing radiation. Figure 1.8 shows Ionizing radiation has a short wavelength and carries greater energy, which can induce DNA strand breaks and mutations that can result in cancer. Non-ionizing radiation, however, possesses sufficient energy to cause molecules' atoms to vibrate at high wavelengths or

to move about within them. Ionizing radiation is frequently produced by radioactive materials, where unstable atomic nuclei with excess energy spontaneously emit, or rays due to their constant decay rate and half-life. [10].

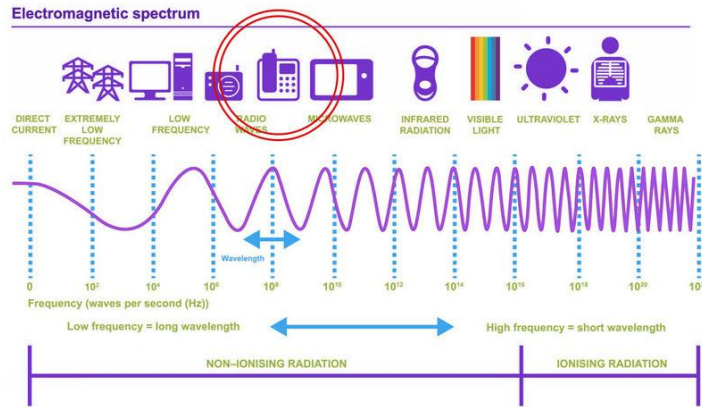


Figure 1.8: The Frequency of Ionizing and Non-Ionizing Radiation [11]

α -radiation, which consists of a pair of protons and two electrons, has the greatest ionization potential but the least penetration. As seen in Figure 1.9, it cannot enter human skin, but it can cause harm when ingested or inhaled. Smoke detectors, pacemakers, and various types of cancer are all treated using alpha radiation. β -Radiation has high energy electrons or positrons with moderate ionization and penetration. It can pierce through human skin, as seen in Figure 1.9. In tracers, beta radiation is used to monitor film thickness and for medical imaging. γ -Radiation, which has the lowest ionization and greatest penetration, is regarded as high-energy electromagnetic energy. As seen in Figure 1.9, it has the capacity to completely penetrate human skin and tissue, causing cellular damage. It is utilized for sterilizing medical equipment, testing equipment, and treating cancer. It is employed in the treatment of cancer, equipment testing, and sterilization of medical devices. [12].

Any substance that receives an ionizing radiation dosage has its energy expressed in mass units. The quantity of energy that is concentrated in tissue as a result of exposure to ionizing radiation is known as the absorption dose. Milligrays (m Gy) are used to measure the absorbed dose. For every organ, the equivalent dosage, which is expressed in millisieverts, is determined (mSv). Whereas an equivalent dose discusses the effects of radiation on a tissue, an absorbed dose describes the energy deposit in a tiny tissue. The effective dose, expressed in millisieverts (mSv), is a computed figure that accounts for three factors: the overall amount of radiation absorbed by the body's organs, the

proportionate level of damage caused by the radiation, and the radiation sensitivity of each organ. Importantly, high gamma radiation doses can build up over time, causing constant exposure to certain of the big dose side effects [12,13], as seen in Figure 1.10.

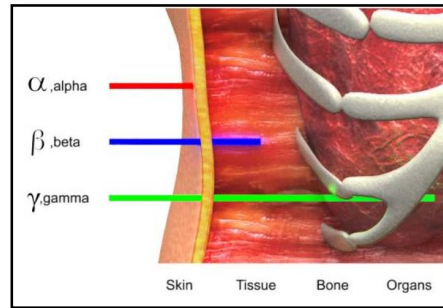


Figure 1.9: Radiation Rays Effect on The Human Body [13].

Natural radiation occurs from a variety of sources, including more than 60 naturally occurring radioactive substances that can be found in the air, rocks, soils, sediments, minerals, and plants. The amounts of these substances vary based on the geological properties of a particular region. Rocks emit radon, a naturally occurring gas. [12].

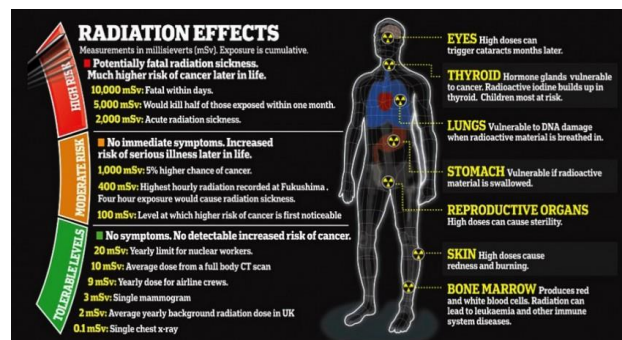


Figure 1.10: Deterministic Biological Damage after Radiation Exposure [14]

1.9 BACKGROUND OF THE RESEARCH STUDY

LPG is a flammable gaseous hydrocarbon compound formed mostly of propane (C_3H_8), butane (C_4H_{10}), and isobutene (C_4H_8), or even a combination of these, and liquefied at ambient temperature and moderate pressures. It compresses linked gas before cooling it using refrigeration. It is maintained under pressure as a liquid in cylinders or tanks. This LPG may be utilized whole or split into its three main components: propane, butane, and isobutene. About 60% of it comes from natural gas, and the other 40% comes from refining crude oil [15]. Around 15% of all oil is utilized in gas-fired power plants, where nearly 3 1012 kg of crude oil and 1012 m3 of natural gas are generated globally [16]. LPG has a high "heating value," or caloric content, and may produce a

lot of heat energy. Every year, more people throughout the world desire LPG. The US, EU, and nations in Northeast Asia, including China, Japan, and South Korea, are the biggest importers of LPG. However, the Middle East, West Africa, and Norway are the top exporters. In contrast to China's 7.1 million tons in 2014 and 4.2 million tons in 2013 [17], the United States exported about 14 million tons of LPG in 2014 [16]. Liquefied petroleum gas (LPG) has become a crucial and conveniently transportable energy source. It is typically used for cooking in homes. LPG is carried from refineries to LPG bottling plants in Bangladesh, India and many other countries by truck tankers, pipelines, and other means. It is then filled in tiny cylinders and delivered to households. The number of LPG bottling facilities has expanded due to the growing demand for tiny home LPG cylinders. LPG bottling operations are made to function safely under typical circumstances. Small cylinders in bottling companies, pump/compressor storage locations, and LPG tank farms are all vulnerable to accidents with cascade effects [18–20]. To find even tiny leaks, LPG is combined with an unpleasant chemical like mercaptan. LPG is particularly dangerous because to its extremely low LFL and low boiling point (-20 to -27 °C). The LFL and UFL have respective vol/vol percentages of 1.8% and 9.8% of gas in the air, an auto-ignition temperature ranges of 410 – 580 °C, and a heating value of 50 MJ/kg [21]. Explosives and rocket engines, fuel bubbles, and a vessel filled with a flammable liquid were all used in experiments on the growth and spread of fireballs that produced a melting liquid-expanded vapor explosion [21, 22].

Nuclear radiation is ubiquitous in our environment. It originates from both natural and artificial sources. The maximum amount of background radiation originates from natural sources. On the other hand, the increasing use of radioactive isotopes and artificial radiation in nuclear installations, the petroleum industry, agriculture nuclear medicine, etc. is according to the increase in background radiation in our environment. Ionizing radiation is frequently produced by radioactive materials, where unstable atomic nuclei with surplus energy spontaneously generate α , β , or γ rays based on the constant decay rate and half-life. Ionizing radiation has a lower wavelength and contains more energy. If a radioactive source emits or inhales alpha particles, the alpha particles are thought to be hazardous internally. [23].

Radionuclides and heavy metals are released by geological formations and are transferred into the ecosystem through water, soil, and sediment [12,24]. Due to anthropogenic activities like industrialization, massive industrial waste disposal,

increased agricultural inputs (such as fertilizers, fungicides, pesticides, herbicides for crops, irrigation water, etc.), and mining, the environment has become more contaminated with these heavy metals and radionuclides [12, 13, 24, 25]. These elements can enter the food chain from the environment via bioaccumulation and biomagnification [25-27]. Many factors influence radioactive movement and mobilization into and within the environment, include psychological, biological, and geochemical modifications to soil, air, water, and flora, as well as specific radionuclide interactions with plants and other species in which they accumulate. [26-28].

People can be affected by various complex diseases by ingesting this contaminated vegetable or inhaling/directly touching of contaminated soil [29-31]. The central nervous system, blood components, lungs, liver, kidneys, and other essential organs may all be harmed by heavy metals, which can lead to mental illnesses and promote a number of medical problems. In addition to disrupting nucleic acids, causing mutations, and mimicking hormones, prolonged exposure to heavy metals or chemicals can also alter the endocrine and reproductive systems and ultimately result in cancer [32]. A radioactive gas that is chemically inert is radon. In that instance, radon won't be oxidized or have its radioactivity or form altered by combustion. It will be expelled from the body without any direct health effects when it enters the body through inhalation. The danger from radon, however, comes from the radioactive byproducts of its decay, which can build up in the lungs after inhalation and include lead, bismuth, and polonium [33]. The total effective dose accumulated in the human body via inhalation and ingestion of terrestrial radioactive substances is approximately 310mSv, and the same result is obtained for radioactive concentration in body tissue. [23].

1.10 MOTIVATION OF THE RESEARCH

This study focused on the source of leakage during the bottling process, where the LPG can be released. Insufficient information is available on the distribution of radionuclides in the LPG bottling plant and environment. And these radionuclides affect the workers of LPG bottling plants, the environment and public health. That's why it should be necessary to determine the radionuclides and heavy metals contained in the liquefied petroleum gas and contaminated soil. along with their impact on the workers of the LPG bottling plant and the environment. Therefore, this research study aims to analysis the energy consumption (LPG) related to safety issues and develop a safety method to reduce energy losses. And to show the negative impact on workers and other peoples'

health and environment (e.g., air and soil) from exposure to this radioactive liquefied petroleum gas (LPG) and source of LPG (crude oil).

1.11 SPECIFIC OBJECTIVES AND POSSIBLE OUTCOMES

Specific objectives

1. To analysis the affected area due to LPG release and wind velocity
2. To estimate the radionuclides and heavy metals in the soils, crude oil, and LPG used in Bangladesh
3. To assess the analytical data along with the potential health risk assessment.

Possible Outcomes

1. Reduce the energy (LPG) consumption.
2. Maximize the safety awareness for workers, public health and environment

1.12 FLOW CHART OF THE SEQUENCE OF RESEARCH WORKS

A flow chart describing the sequence of work is shown in Figure 1.11

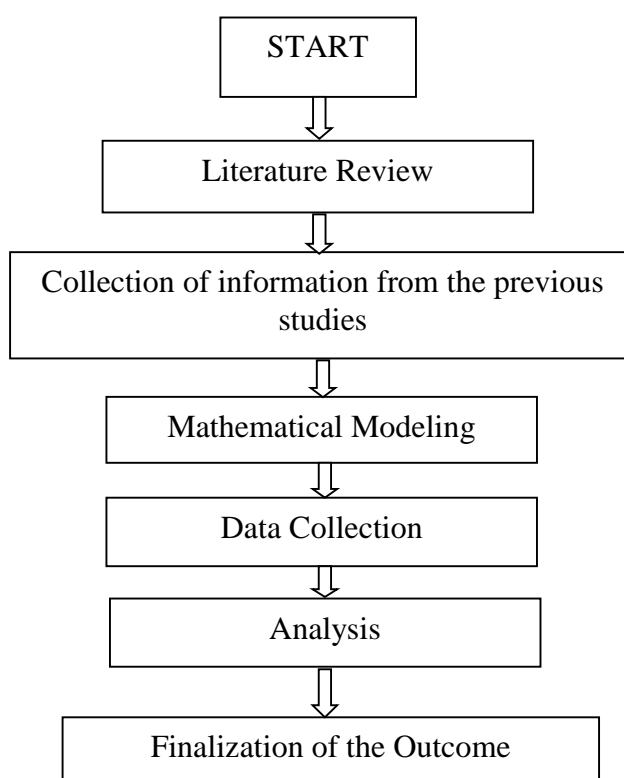


Figure 1.11 Flow Chart of the Sequence of Works

1.13 ANALYTICAL TECHNIQUE USING ALOHA DISPERSION MODEL

ALOHA, an open-source program created by the National Oceanic and Atmospheric Administration and the United States Environmental Protection Agency, was used to

simulate the dispersion of chemical vapor and unintentional discharges of dangerous substances. It offers a variety of accident scenarios for the user to choose from and uses an appropriate source algorithm to quickly put material into the environment [34]. It was based on the continuous, buoyant air pollution flume model with Gaussian dispersion. For more than 900 compounds, the model can replicate the dispersion model [35]. ALOHA can only assess the dangers of substances that go airborne. It includes models for calculating the rate of chemical escape and vaporization from confinement. ALOHA includes models for source intensity, Gaussian dispersion, and heavy gas dispersion. It can also solve the heat radiation and overpressure problems [36].

The research is concerned with the hazards caused by LPG emissions during cylinder bottling. In order to evaluate the risk of fire and explosion from different LPG compounds under varying wind velocity and a fixed volume of LPG released into the environment, the Areal Location of Hazardous Atmospheres (ALOHA Version-5.4.7) models were employed.

1.14 TYPICAL PROCEDURE FOR NEUTRON ACTIVATION ANALYSIS

Timely and adequate analytical support to evaluate plant samples is one of the essential needs for effectively determining the level of contamination, expulsion, and remedial activities at contaminated waste sites. Historically, it has been difficult to get high-quality sample analysis outcomes in the time frame necessary for successful data exploitation [37]. In that case, several spectrometric techniques (e.g., XRF, NAA, AAS, ICP-OES, and ICP-MS) are applied to analyze elemental impurities [38-42]. In this study, neutron activation analysis (NAA) is used with a HPGs detector to identify the toxic metals in the LPG and soil. It is a sensitive way of assessing the chemical composition of substances that uses neutron capture in the nucleus of the test sample to produce radioactive nuclei. Two types of gamma radiation are generated during these reactions: prompt gamma radiation, which is emitted instantly after neutron capture, and delayed gamma radiation, which is emitted simultaneously with the radioactive decay of excited nuclei until it is stable. Neutron activation analysis determines the total mass of elements in the sample. Because INAA, formerly known as non-destructive NAA,' does not need sample disintegration, there are no losses owing to partial digestion, precipitation, or wall adsorption effects, nor is the technology contaminated by the solvents employed [40]. IAEA-approved reference materials, such as IAEA-Soil-7, IAEA-RM-375, and IAEA-RM-Soil-6, are used to derive the calibration factors

for quality control of the results in order to guarantee the accuracy of this analytical procedure [43, 44]. For short irradiation, irradiate the sample 5-30s, and for long irradiation, irradiate the sample for about 1-8 h, where the neutron flux rates are 10^{16} - $10^{18}\text{m}^{-2}\text{s}^{-1}$ E(Hamidatou et al., 2013)[45]. The samples are typically measured for an hour in a system integrated with high-resolution gamma-ray spectrometry in order to identify the short half-life nuclides. The samples are reexamined in a few days (5-7) to determine which elements have longer half-lives. The samples are tested again around three weeks following irradiation to identify the long-lived radionuclides [46]. The multichannel analyzer's energy spread will be decreased by about 30% over 4096 channels, resulting in a gamma line of ^{60}Co with a small background shield and 30–40% efficiency. Radionuclides in the irradiated sample can be identified by gamma-ray counting for irradiated samples after decay time, with a measurement period of 2000–86400s [26, 47,48,49]. A number of detectors, including scintillation detectors (NaI, CsF, and ZnS), gas-filled detectors, and semiconductor detectors (based on Si, Ge, CdTe, and GaAs crystals), can be used to detect and measure gamma rays [43]. This spectral peak is sent to the computer through a multichannel analyzer and examined by specialist software [37, 44]. Figure 1.12 illustrates the analysis's process.

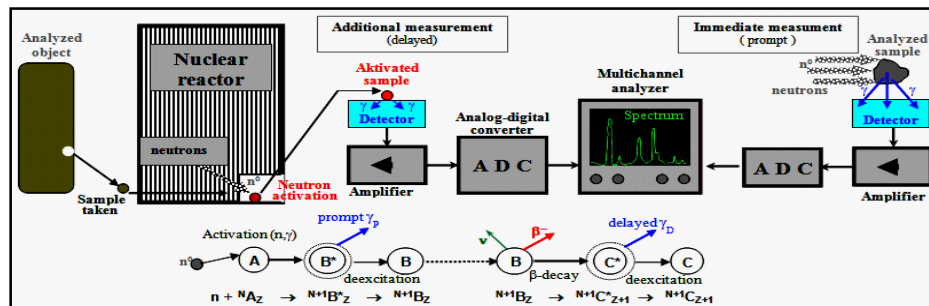
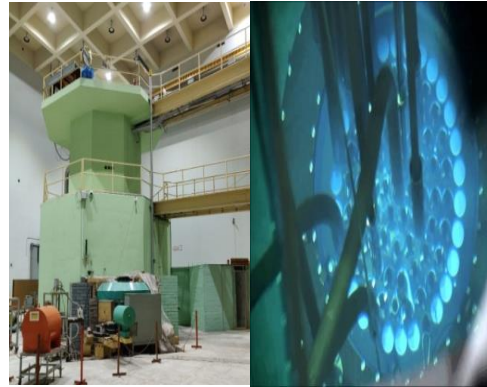


Figure 1.12: Typical Procedure for Neutron Activation Analysis[40].

1.15 TRIGA MARK-II RESEARCH REACTOR

Some reactors expose samples to neutron irradiation to produce radioisotopes for various applications. The object can be put in a reactor-mounted treatment vessel, and cadmium can be employed to filter off thermal neutrons if epithermal neutrons are desired for the irradiation. The exterior and interior views of the TRIGA Mark-II research reactor at Savar, Dhaka, are depicted in Figure 1.13. It is a radioisotope thermoelectric generator in the form of a tank that is used for learning, evaluation, and isotope production. General Atomics in the United States designed and built the reactor.

The reactor installation began in late 1980 as a non-turnkey project. A reaction vessel, reactor core, fuel, control rod, moderators, reflectors, refrigerants, and reactor shield make up the TRIGA Mark-II research reactor.



Outer View

Inner View

Figure 1.13: The Savar Research Reactor for TRIGAMARK-II is in Dhaka.

1.15.1 Facilities for Irradiation from the TRIGA MARK-II Reactor

For use in research, teaching, and the production of isotopes, AERE's TRIGA Mark II research reactor is built to create high-intensity ionizing radiation fluxes. The following facilities can be used to conduct experiments using the TRIGA MARK II research reactor:

- System for pneumatic transfer
- (Lazy Susan) Rotary specimen rack
- Tubes for neutron beams
- a hexagonal cutout in the core's middle
- Central irradiation tube that is dry
- Triangular cut-outs in the core
- Thermal column for future use. (3 MW TMRR, 2003)

1.15.2 Pneumatic Transfer System

The pneumatic transfer system is used to irradiate monitors that generate radioisotopes with brief half-lives; the transfer time is around 4.6 seconds. A pneumatic transfer mechanism swiftly transports a specimen to and from the reactor core to produce an extremely short-lived radioisotope. Ejected into the core, "Rabbit's" polyethylene specimen capsule is landed vertically in the middle of the core. After a predetermined amount of time, the specimen capsule is automatically discharged.

Table 1.3 TRIGA MARK-II Research Reactor, AERE, Savar, Dhaka Values of Neutron Flux (n/cm²/cm) (Glascock, 2004).

Different position	Epithermal	Thermal
Average flux in the reactor core	1.1×10^{13}	5.3×10^{13}
Central tube	1.5×10^{13}	5.56×10^{13}
Rotary rack (at the bottom)	0.26×10^{13}	0.75×10^{13}
G- ring	1.0×10^{13}	2.0×10^{13}

1.16. GAMMA RAY DETECTION

After being subjected to radiation, the samples and standards are placed on the HPGe (High Purity Germanium) detector. Using an HPGe detector and a Digital Spectrum Analyzer, the experimental samples' gamma ray emissions were discovered. The analyzer (DSA-1000) with Canberra Detector Interface Module (DIM) is outfitted with many tools, including a PC-based Multi-Channel Analyzer (MCA) Software-Genie 2000, a high voltage power source, a pre-amplifier, and an analog to digital conversion (ADC). Figure 1.14 depicts the schematic layout of the gamma-ray monitoring system.

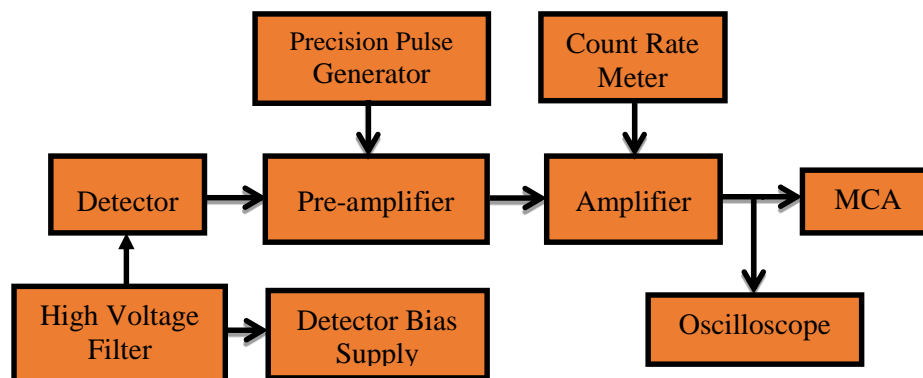


Figure 1.14: Block Diagram of the Detection of Gamma Rays [50]

1.16.1 Germanium (HPGe) High Purity Detector

A semiconductor detector, related electronics, and a computer-based multi-channel analyzer are typically the components of the apparatus required to measure gamma radiation from radioactive materials. Hyper-pure or intrinsic germanium (HPGe) detectors are frequently used. These detectors can operate at liquid nitrogen temperatures by enclosing the germanium crystal in a vacuum crystal that is thermally connected to a copper rod or "cold finger."

One kind of semiconductor detector is an HPGe (High Purity Germanium) detector. The gamma rays that the product's nucleus releases are picked up by the HPGe detector.

As an HPGe detector has a greater resolution than an NI crystal, it is a highly precise instrument that is frequently used for gamma spectroscopy analysis. Semiconductor detectors provide accessible, free-charge carriers that may be employed for incident radiation detection and measurement. Figure 1.15 depicts the Configuration of The HPGe Detector.

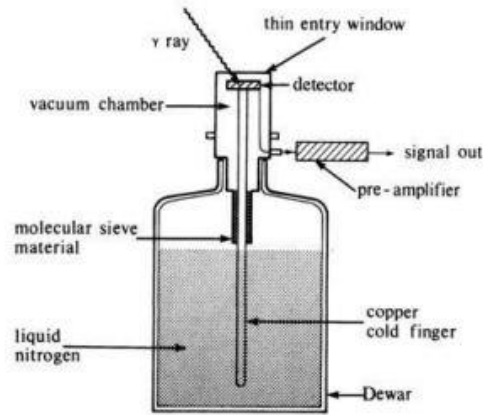


Figure 1.15: Configuration of The HPGe Detector [50]



(a)



(b)

Figure 1.16: (a) HPGe Detector System and (b) Gamma-ray Counter at BAEC Savar, Dhaka

There are two somewhat straightforward geometrics for HPGe detectors:

1. Planer detector, where the electric field is comparatively uniform
2. The coaxial arrangement, where the electric field varies inversely with the radial separation from the detector axis.

A Ge (Li) detector of the same size and form exhibits the same gamma ray detection efficiency and response function as the HPGe detector. The components of the HPGe gamma spectrometry system are as follows:

HPGe detector:

- a) Cryostat
- b) Liquid Nitrogen (LN₂)
- c) Pre-amplifier

Digital Gamma Spectrometer

- a) Amplifier
- b) High voltage unit
- c) Analog to Digital Converter (ADC)

Shielding arrangement

The final three components are combined inside a box. Canberra's product is known as DSA, while ORTEC's offering is known as DSPEC.

1.17 OUTLINE OF THE THESIS BOOK

Chapter 1 describes some basics on LPG, radiation and their impact on health, specific objectives with possible outcomes of this current experimental and analytical analysis, and the layout of the thesis.

Chapter 2 included a review study on this topic conducted by searching the most recently published journals. Significant work is involved in the hazards of LPG distribution, radionuclides in LPG, and soil. This chapter is closed with a discussion of the potential research gaps in radionuclides and elemental accumulation in LPG.

Chapter 3 describes the study area and the specific purpose of the study, sample collection and preparation, the INAA technique, the INAA irradiation procedure, and the gamma-ray HPGe detector.

Chapter 4 evaluates the concentration of heavy metals and radionuclides in the collected samples (crude oil, LPG and soil). Then the findings were compared with the data from the published journal, including USEPA and UNSCEAR reporting recommended values.

Chapter 5 calculates the potential risk assessment related to the environment and human body, especially workers, due to LPG leakage from bottling plants and distribution. concludes the thesis work based on the experimental and analytical findings, as well as conveys the recommendation for future work in this research are

CHAPTER II

LITERATURE REVIEW

2.1. CURRENT STATUS OF LPG IN BANGLADESH

Bangladesh, with a population of more than 160 million people, requires a precise and comprehensive plan for supplying primary cooking fuel. The existing system relies heavily on natural gas delivered via an antiquated pipeline supply chain. But, with the government's support, LPG has begun to progressively take control. About 30 million people are thought to live in Bangladesh. Large cities use natural gas as their primary fuel source, whereas smaller cities use electricity, LPG, kerosene, firewood, or a combination of all of these fuels. The government has already stopped all new natural gas installations because there is no upstream development of natural gas and is promoting LPG as a replacement. LPG will therefore gradually gain traction in the kitchen, similar to how it has in many other nations, and the nation faces a formidable distribution dilemma. Not only are LPG firms benefiting from an effective, secure, and reliable supply chain, but the whole country is as well [9].

In 2017, more than 700,000 MT of LPG were imported and sold locally, which is approximately twice as much as in 2016. The sector saw a slowdown in the last few months (end of 2017 to early 2018), which could have been caused by the high purchase price, rising freight and charges, and a rapid rise in supply due to new LPG firms. So, it is safe to say that at this time, the supply is practically meeting the demand, which is now around 800,000 MT. Market sources report that there are currently 48 LPG license holders. There will be the construction of 23 LPG terminals, followed by 16 more, and 43 filling stations. In other words, the supply side is currently growing swiftly to meet the demand at the national level. Consumers should take note of this to ensure that LPG is available and reasonably priced [9].

Allowing the LPG market to expand following the global market shows that the administration has adopted a very tenable stance (free market policy). As there will be a greater supply of LPG firms on the market, there will be more competition, and eventually, only the most effective players will be able to dominate. The implementation of rules and regulations, organized distribution channels, service quality, and awareness raising should now get underway. LPG is a very safe fuel when

it is used in systems that are entirely enclosed from the point of supply to the point of consumption by the end user. LPG storage and handling procedures have been well developed over many years, leading to safe usage in a broad spectrum of uses and marketplaces around the world [9].

2.2. PROPERTIES AND HAZARDS OF LP GAS

Although it releases CO₂ into the environment during burning, being a fossil fuel, it burns quicker than others and is thus environmentally friendly and efficient. Due to these characteristics, LPG is a viable alternative to traditional fuels as well as an ecologically benign fuel. Liquefied petroleum gas is becoming increasingly popular due to its low cost and low emissions [51]. Like other energy sources, LPG can be seriously dangerous if improperly stored. Explosions and flames are the most hazardous characteristics of LPG. Table 2.1 and Figure 2.1 highlight the most critical features of LPG that make it dangerous [46, 47].

Table 2.1: Properties of LPG [46]

Physical properties	n-Butane	Propane
Chemical formula	C ₄ H ₁₀	C ₃ H ₆
Liquid density	583	506
Flash point (°C)	-60	-104
Upper explosive limit (vol. %)	8.5	9.5
Upper explosive limit (vol. %)	1.9	2.3
Val. vapor per vol. liquid	235	269
Relative vapor density	1.07	1.55
Specific energy (KJ/Kg)	49.40	49.83

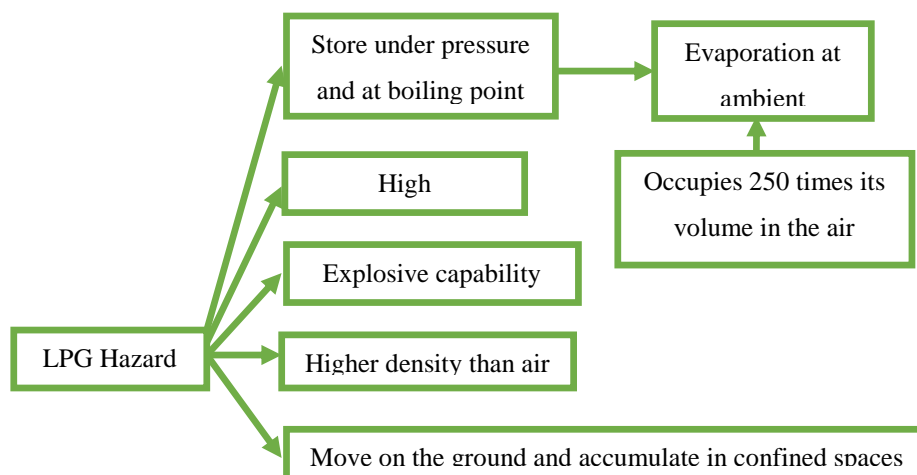


Figure 2.1: Properties of LPG that Make it Dangerous [46]

The facility should be fireproofed if there is a danger of jet fire since this form on fire has a significant effect for damaging nearby instruments owing to its high heating value. The fireball that the BLEVE phenomena typically produces has a big radius and a strong heat flux across a sizable area, all of which contribute to its enormous damage. Design and installation faults and management and organizational issues each contributed to 25% and 23% of accidents, respectively [48]. When LPG tanks are exposed to fire, they deteriorate quickly. It is critical to respond promptly to stabilize the situation. The BLEVE incident is the LPG storage tank accident with the greatest overall impact. Therefore, it must be specifically avoided. Figure 2.2 shows other consequences of the LPG incident.

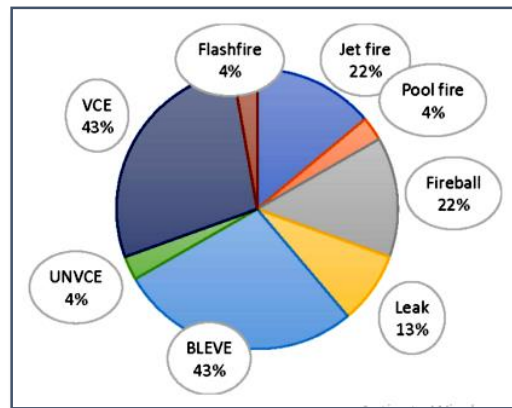


Figure 2.2: Final Consequence of LPG Accidents [48]

A blast wave can be constructed based on the speed of the flame front, a phenomenon described as vapor cloud explosions. Wind speed, path, flow rates, gaseous density, and Mixing at the source is only one of the meteorological parameters that have an impact on VCE. A gas explosion occurs when the combustion of a fuel-air mixture, fuel/oxidizer mixture, or fluidized gas cloud results in a sudden rise in pressure. Gas explosions can happen in pipes, buildings, maritime modules, open process areas, limited places, or the industrial process itself [49].

As seen in Figure 2.3, an explosion requires the discharge of gas. Then, ignition must be present to ignite the expelled gas, which might result in a fire or an explosion. Most vapor cloud explosions at onshore and offshore petroleum processing plants would be classified as deflagrations [49]. When exposed to outside heating sources, LPG containers have pressure-relieving valves that allow LPG to escape to the atmosphere or a flare stack. If a fire is permitted to burn for a long enough time and with a strong

enough intensity, it may result in a boiling liquid expanding vapor explosion (BLEVE) within a tank. The storage of several exceedingly big containers is a common problem for chemical and refinery companies. Frequently, tanks are built so that the product will vent before dangerous pressure levels are reached [52].

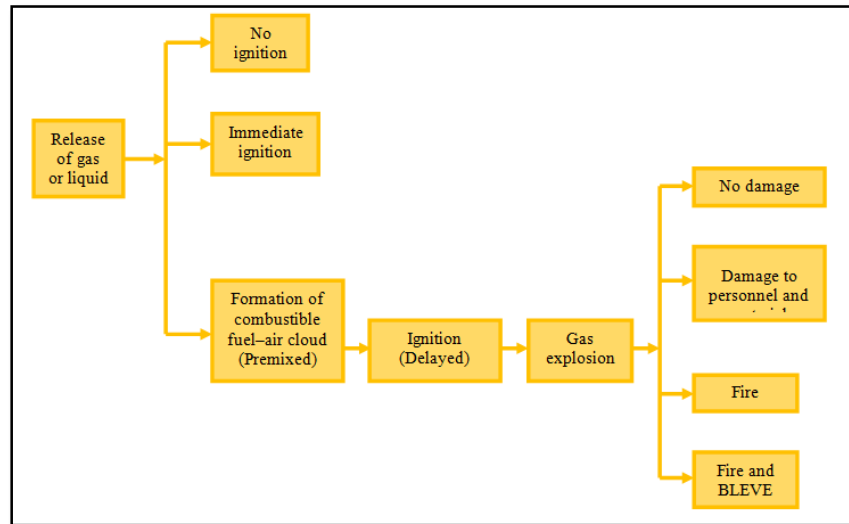


Figure 2.3: Typical Repercussions of Flammable Gas or Evaporating Liquid Leaks into the Atmosphere [49].

2.3. RADIONUCLIDES ELEMENT IN LPG FROM CRUDE OIL

The oil and gas are associated with the ^{238}U and ^{232}Th decay series radionuclides, which create radioactive elements with varying half-lives and activity concentrations based on the type of rock and the power of releasing radiation present throughout the earth's crust.

Natural gas contains radon; the average radon concentration per liter of gas globally is 1.5 Bq/L. When liquid petroleum gas (LPG) is bottled, long-lived radon offspring (^{210}Pb and ^{210}Po) collect in the LPG processing machinery, exposing maintenance personnel to low levels of radiation. The annual dosages of crude oil and natural gas for each individual are calculated to be 10 nSv and 1 nSv, respectively. The estimated doses are entered into the human body from radioactive particles and radon gas through inhalation [53]. One of the radioactive gaseous radionuclides in the ^{238}U decay series, present in natural gas utilized in the petroleum industry and produced directly from the alpha decay of ^{226}Ra , is ^{222}Rn , according to Chanyotha et al. [23]. The human body is exposed to this radioactive gas, which has a half-life of 3.8 days [33]. The distribution process of the NORM from the recovery process is shown in Figure 2.4.

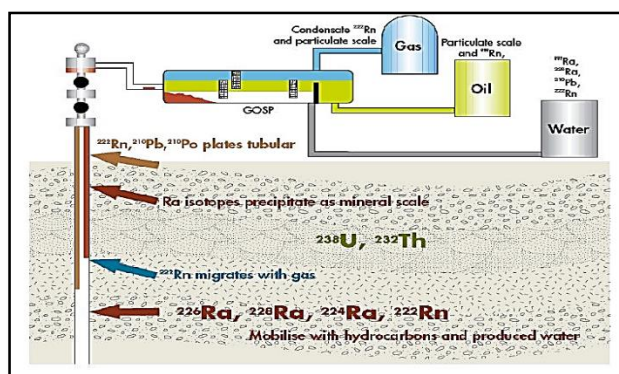


Figure 2.4: Distribution of NORM from the Recovery Process [54].

Radium and radon are pumped to the surface with crude oil extraction, while uranium and thorium rarely dissolve in water. The concentration of ^{222}Rn in water producing petroleum is 18.5Bqdm^{-3} , and different cations, such as barium and strontium, have lower bicarbonate solubility of radon in sulfate, chloride, or water. On a global scale, it is anticipated that the radioactive concentration in water released into the atmosphere will be 10Bq/l . These levels of radium are around three times greater than those found naturally in drinking water or ocean. On the pipe scale and in the waste mud, the levels of radon and radium depend on three things: the level of Ra in the topsoil, the kind of treatment used for extracting oil or gas, and the nature of the water component. As seen in Figure 2.5. During scale development, the majority of the radium radionuclides are actually concentrated in the aqueous phase. As a result, the activity concentration measured on individual mud and solid scales is substantially higher than the activity concentration recorded in water produced by the oil sector. Sulfate scales, such as BaSO_4 , sometimes known as barite, are the most common types of scales found between oil and gas installations. Barite often has a colorless or milky white appearance; however, it can also be any hue depending on the impurities entrained in the crystals during crystallization. The significance of barite in various applications is due to its high concentration. Radium sulfate, radium carbonate, and occasionally radium silicate is used to create scale due to radium's significant chemical resemblance to barium (Ba), strontium (Sr), and calcium (Ca). As was previously indicated, the sulfate-rich seawater and the Cl^{-1} rich generated water together increase the potential for scaling, as seen in Figure 2.5.

According to Awwad et al. [54], the pressure, temperature, and acidity of the oil and gas produced on the surface from the reservoir by other radionuclides all have an impact

on the conditions in which radioactive material is transported or decays. When producing LPG, a mixture of oil, gas, and water naturally contains radionuclides, which



Figure 2.5: Scaling of the Interior Pipe of LPG Recovery Process [54].

are transmitted and deposited on the scale, sludge, and scraping. Additionally, they leave a thin layer of residue on the interior surfaces of LP gas processing equipment and tanks. The degree of NORMs is significantly influenced by the geological structure, and it has been found that the submission differs from one site to the next [33, 54]. Older mud occasionally contains ^{228}Th radionuclides, which are byproducts of the disintegration of ^{226}Ra [55].

2.4. LPG BOTTLING PROCESS HAZARDERS

2.4.1. Hazarders LPG and Safety in Bottling Plant

Before bottling in every sector, safety comes first. Safety requires the use of personal protection equipment (PPE) while working. On average, the risks include fire, sound pollution, hand and limb injuries, and leaks. When filling in the carousel, LPG leakage from the cylinder is possible. LPG leaks can also happen when screws are undone. During the pull-up of a cylinder on an online chain conveyor, a hand or leg may be harmed. The process of bottling contributes to noise pollution [56-58].

In today's world, energy security is crucial. The automated filling method is more efficient and safe. Before refilling, the cylinder must be checked visually. Before filling, washing and drying are carried out if required, the "O" ring in the cylinder valve must be examined to prevent gas leaks, and it must be replaced if it is missing. A modern machine carousel fills the cylinder with LP gas once the cylinder is given body weight. Several cylinders may be filled simultaneously by the automated carousel machine. To confirm that it is filled to the required level, the cylinder was verified using an automated weight-checking scale. The LPG filled cylinder's valve leak should then be examined for security and safety. In order to increase safety, it is important to attach the thermos sleeve and place a safety cap on the cylinder valve if all operations are

successful. The filled cylinders are then held in storage until they are distributed. Wearing Personal Protection Equipment (PPE) while filling the cylinder is mandatory [59]. To contain LP gas, various cylinder sizes are available. When weight is an issue, aluminum and plastic are posing as attractive alternatives to steel. Another enticing alternative to steel is composite LPG cylinders. LPG cylinders can hold between less than 1 kilogram and 50 kilograms [60]. Because of its extreme flammability, LPG poses a fire and explosion risk from the time it is manufactured, distributed, and transported until it is used and disposed of [17]. The most dangerous explosive hazard connected with LPG is boiling liquid expanding vapor explosion (BLEVE), which may cause highly damaging blast waves [61]. LPG can escape as a gas or a liquid. LPG vapor will condense in small spaces and low-lying regions since it is heavier than air. An oxygen-deficient environment that entails a risk of asphyxiation may develop as a result of LPG vapor buildup. The gas has the potential to ignite or explode when it comes into contact with an ignition source. Other dangers include poor ventilation, narcotic effects from carbon monoxide created by burning, and cold burns from LPG should not be applied to the skin. [17,61, 62]. Safety could be jeopardized by inadequate quality control in the LPG manufacturing and refining operations., creating risks during distribution and usage. Because negligence at any phase might result in danger, it is imperative to control and oversee the procedures involved in bottling to reduce possible risks throughout shipping, distribution, and ultimately consumer consumption. Additionally, it is essential to take safety precautions for the manufacturing personnel [61, 62]. Most of the world's LPG industry uses an automated bottling process. All industries also have a manual method of filling the cylinder. The manual filling is necessary when the automated technique fails. If a repair is required, the cylinder is kept for later use. If it does, the cylinder is put on the chain conveyor line for filling. The washing unit is the device that cleans incoming cylinders. Several high-pressure water jets are used to deep clean the outside of the cylinder of dirt, dust, stains, etc. Most enterprises have built up equipment for online washing units. In some businesses, the cylinder's outside is washed using a washing machine. Check the "O" ring in the cylinder valve before filling it. To reduce LP gas leakage an, "O" ring is necessary. After washing and drying, most industries install an "O" ring in the cylinder valve if one is missing. The specified weight of LP gas is added to the cylinder using a Tare weight unit. Body weight is not the same for all cylinders. As a result, before filling, the cylinder's body weight must be established. Due to the circular filling heads used by carousels, an empty cylinder

enters the vehicle, is filled as it rotates around it, and then is expelled from the vehicle full. There could be fewer or more heads on the carousel. The cylinder might be filled automatically by this carousel. Any LPG industry needs manual scales as well [63]. A leak detector is a device seen in a wide range of industries to find flaws that are emitted by things. It is used in the LPG business to detect leaks in LP gas-filling cylinders. There are many types of leaks, including valve, bottom, and cylinder head leaks. A safety cap is a type of protective cap used on cylinder valves. It is used to prevent gas leaks [60, 63].

2.4.2 LPG Accident from Storage Tank

A small leak can cause a lot of harm because LP gas storage tanks are held under pressure and above the boiling point [49]. In petroleum storage and dispensing plants, LPG is a popular and often used household fuel that is provided and held in a totally cooled form inside a pressure vessel under pressurized conditions.

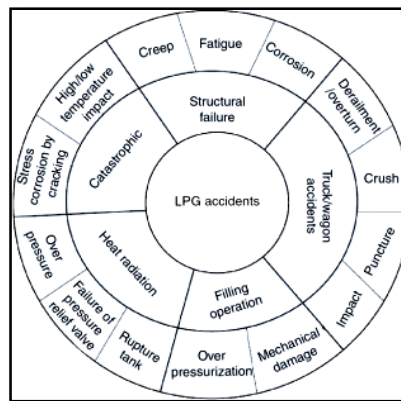


Figure 2.6: Numerous Potential Incidents While Handling LPG [19].

Because it is either pure propane gas or contains a significant amount of propane, LPG is sometimes referred to as liquefied propane gas. Overall, the amount of LPG varies by nation and refinery depending on the purification processes of splitting, hydrogen processing, crude separation, and refining. Many different types of vessels are used to store and transport LPG, including enormous bullets, rail wagons, and road tankers [19, 64]. Recent observations of handling, storing, and exporting LPG have shown a large number of fire and explosion accidents. An LPG container can malfunction due to mechanical damage or overfilling storage, which can lead to weld failure and vessel cracking, including mechanical impact. The riskiest actions in LPG handling include loading and unloading [19, 65]. LPG incidents are most prevalent at storage depots, processing plants, and during transportation, as shown in Figure 2.6. A very well-

liquefied gas intake line enters the container from the top for LPG cartridge storage. Moreover, the top of each tank has the vapor exit line for the gas's direct use in the plant removed. Two control valves connect the outflow line and liquid release line to the bottom of the LPG tanks, with the latter's end terminating outside the shadow of the tank. The LPG bullet storage is outfitted with safety gear, such as rotational gauges (devices to gauge the amount of LPG) and temperature, pressure, and pressure gauges. Figure 2.7 depicts the locations of the most likely failure points in LPG bullets. Even if all conditions are ideal and all safety measures are taken into account during construction and operation, LPG storage tank fires can still have devastating repercussions. The catastrophic tank collapse, in this instance, will result in BLEVE, fireball, VCE, or any combination of these [48].

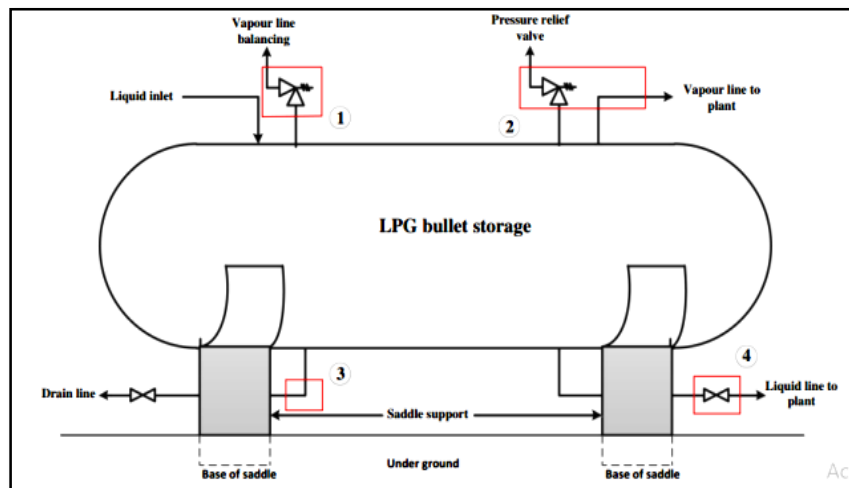


Figure 2.7: The Bottling Plant, a Typical LPG Bullet Storage Tank without a Bund area [20].

The bottling plant's operator is in charge of the LPG pump or compressor room. A leak in the discharge line causes the LPG pump to shut off at 14.34 bar of pressure [20].

According to Demirbas et al. a metal alloy (granular or particles) and hydrogen combine to undergo an exothermic reaction [66]. Heat must be supplied before the hydrogen can be released from these metal particles in order to increase pressure inside the containers. When a metal hydride absorbs hydrogen, heat is generated [66]. According to Pula et al., combustible material leakage or spillage can result in a fire that can be initiated by a variety of different igniting sources (sparks, open flames, and so on). Depending on the kinds of discharge events, four different forms of flames can develop in an offshore environment: pool fires, jet fires, fireballs, and flash fires. One of the four known

categories is always represented, among others, by flares, sea surface flames, and flowing liquid fires. He also said that an explosion is described as a quick, powerful release of energy that results in a fatal boom. Depending on the type of energy released into the environment, an explosion can be characterized as physical, chemical, or nuclear. A gas explosion is created by the fast formation and expansion of gases as a result of the rapid burning of a combustible material. A gas explosion is typically described by the degree of confinement and constriction in the region surrounded by the cloud of gas. Congestion in the form of obstacles raises the flow's turbulence level, resulting in more equally accelerated motion and overpressures [67].

2.5. NORM IN LPG FROM NATURAL GAS PROCESSING

In 1904, NORM published its first report on natural gas and mineral oil. The presence of ^{226}Ra reservoir water from oil and gas operations was recorded in later publications, and in the late 1970s and early 1980s, several findings sparked fresh attention. According to the examination of NORM from numerous oil and gas fields, the solid items found in the downhole and surface structures of the oil and gas extraction facilities—which do not include oil, gas, or water from the source rocks—do not contain the ^{238}U and ^{232}Th . Calcium, strontium, barium, and radium are still present in the water in the formation after the reservoir rock has been dissolved [54, 55]. The result is that the water created comprises the radium isotopes ^{226}Ra from the ^{238}U series as well as ^{228}Ra and ^{224}Ra from the ^{232}Th series (Appendix-A.1 Figure A.1a and A.1b, respectively). Consequently, water that has created in conjunction with gas or oil has three isotopes of radium but not their parents. Because of the accumulation of their long-lived parents ^{238}U and ^{232}Th in the LPG reservoir, they are characterized as being "unsupported." The reduction in pressure and temperature may be greater than the solubility of their mixed sulfate and carbonate products when group II components, particularly radium, are involved in the generated water [54, 55]

If sulfate and carbonate precipitate, scale may form on the inside walls of tubular items, gas wells, gates, pumps, separators, water purification vessels, gas treatment procedures, and oil storage tanks. Opportunities for accumulation in the storage tank of a turbulent flow are provided by centripetal forces and nucleation sites. The mixture of oil, gas, and water also contains ^{222}Rn gas, which is produced by the decomposition of ^{226}Ra in reservoir rock. This radioactive gas travels with the gas-water flow from the production area, and then, according to priority, the dry export gases follow the surface

of the gas line as shown in Figure 2.8. ^{210}Pb and ^{210}Po are also accumulated in LPG during processing from the reservoir [54, 55]

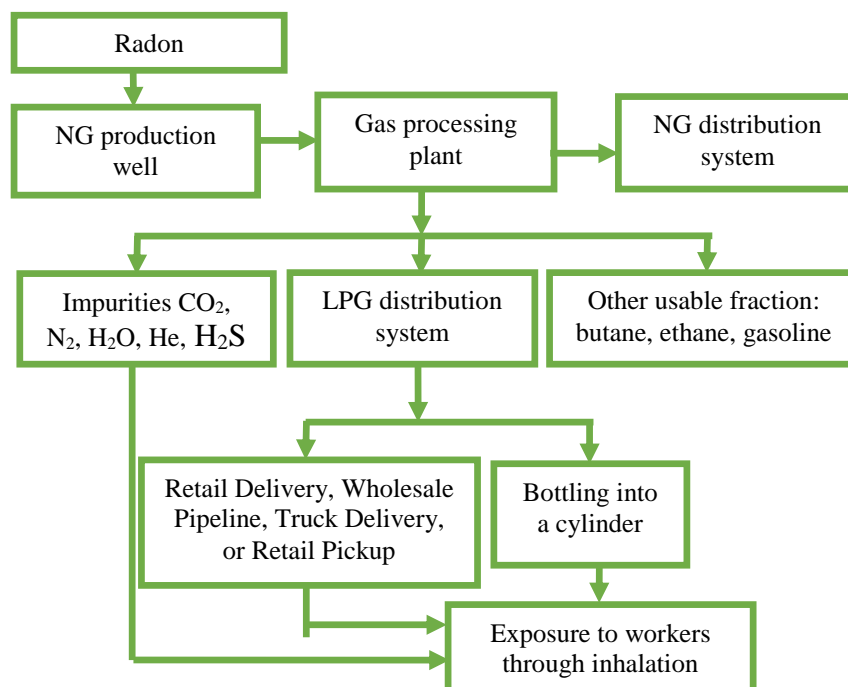


Figure 2.8: Flow Diagram of the Exposure of Radon during LPG Processing [68].

A gaseous hydrocarbon created from crude oil or the processing of natural gas is liquefied petroleum gas. According to several research articles, crude oil is the source of ^{238}U and ^{232}Th series radionuclides in the LP gas. On the other hand, NORMs is associated with natural gas walls. Among these radionuclides ^{222}Rn gas can travel with the gas-water flow from the production region and accumulate in LPG with its decay ^{210}Po and ^{210}Pb [54, 55].

2.6. HEAVY METALS AND RADIONUCLIDES IN SOIL

Heavy metal concentrations have been discovered in many earlier investigations in both the soil where vegetables are grown and in the crops themselves. Appendix A.1 (Table A.1) contains concentrations of the heavy metals they detected in the soil and vegetables during their study. Navarrete et al. proposed that organic matter and accessible phosphorous content in soil properties mostly controlled heavy metal concentrations [69]. According to Lora, heavy metal absorption from soil to plants is a result of the soil's physical and chemical characteristics and is controlled by a number of environmental and societal factors [70]. Cd, Co, Cr, Cu, Pd, Hg, and Zn are known as common heavy metals, while arsenic (As) and antimony (Sb) are now increasingly called heavy metalloids [31]. Heavy metals like copper, zinc, iron, manganese,

molybdenum, nickel, and cobalt are necessary micronutrients but can be detrimental if taken in excess of what plants require [71,72]. Cd, Pb, As, Hg, and Cr are non-essential heavy metals that induce negative impacts and major issues even at low concentrations [73]. Natural processes like volcanic eruptions, spring waters, weathering, and microbial activity as well as anthropogenic processes like burning fossil fuels, operating machinery, engaging in agriculture, and feeding are all ways that these heavy metals are released into the environment [25, 72-75]. The use of pesticides, sewage sludge, and chemical fertilizers that include heavy metal(loid)s can also lead to heavy metal(loid) pollution of agricultural soils [31, 73]. A direct deposit of heavy metals in the soil where vegetables and other crops are grown may result from the uncontrolled open burning of electronic waste and the exposure of heavy metals during the salvage of useable items [76]. Long-term effluents from the disposal of industrial pollutants continually enter water bodies, which causes heavy metals to accumulate excessively in the soil. Because of the abundant availability and lack of fresh water, local farmers in many areas utilize wastewater to irrigate crops, bringing contaminants to crops mostly in urban environments [77]. On the other hand, maximal elements (such as K, Fe, and Zn) are regularly added to the soil in the form of mineral fertilizers, but heavy metal migration and mobility can be affected by chemical and physical soil characteristics (pH, CEC, salt concentration, water, and temperature) [78]. Arsenic enrichment in soils can be caused mainly by agricultural inputs (pesticides and manure), as well as mining and smelting activities [79]. Ejaz et al. evaluated soil-plant-human interactions in heavy metal-contaminated regions of Romania and discovered a considerable gynogenic abundance of higher levels of Pb and Cd. The contaminated soils were neutral to slightly alkaline, with a high organic matter content [80]. Through Cr residues, Cr dust, and Cr wastewater irrigation, modern agriculture continuously releases Cr into the environment, contaminating the soil, harming the soil-vegetable system, and impairing the quantity and quality of vegetables for human consumption [81]. Numerous plant biological processes, including those of maize, wheat, barley, cauliflower, Catullus, and vegetables, are impacted by chromium toxicity [82]. In this situation, the majority of researchers have found Fe, V, Cr, Zn, As, Mn, Co, Cu, Ni, Sr, Mo, Cd, Pb and Hg in soil and LPG, together with their toxicity for human health [25, 78, 83-92]. The presence of radionuclides in the soil where they are planted has also been noted by certain researchers. Appendix A.2 (Table A.2) contains the radioactive concentrations in the soil that were discovered during their examination, together with

information about their detecting apparatus. Atoms that are radioactively unstable and produce ionizing radiation are called radionuclides. Environmental radionuclides can be created by both rock erosion and the deposition of cosmogenic radionuclides [31, 93, 94]. Since NORM half-lives are comparable to the age of the earth, primordial natural radioactivity is still significant today. It can be found in a number of geological formations (such as soil, plants, water, air, coal, phosphate deposits, sediments, and minerals) in a range of concentrations depending on the geochemical properties of a location [95–97]. Primordial radioactive nuclides that are found in the environment spontaneously release ionizing radiation that is very dangerous to human health [98]. The soil, construction materials, air, water, and plants all contain naturally occurring radioactive elements to which the global population is exposed [93]. The most frequent side effects of radiation exposure include cancer and genetic damage, as well as physiological problems such as kidney disease, lung cancer, renal failure, and anomalies in the bones [98-100]. Around 80% of the radiation that humans are exposed to comes from natural sources such radon gas exposure, cosmic radiation, and terrestrial radionuclides. But about 20% of radiation exposure comes from anthropogenic sources like large-scale industrial waste disposal, increased agricultural inputs, medical equipment, mining, nuclear waste disposal, and nuclear weapon testing [94, 96, 101]. The main radioactive sources in soil are the parent series of ^{238}U and ^{232}Th , including natural ^{40}K [96, 97, 102]. The soil containing ^{226}Ra and ^{232}Th is one of the main sources of the airborne ^{222}Rn and ^{220}Rn alpha-emitters. These radioactive gases and the short-lived decay byproducts are the main sources of internal radiation exposure [96, 102]. Moore et al., 1976, demonstrated that human activity may be responsible for up to 7% of total ^{210}Po fluxes in the atmosphere, with increased concentrations in streams and soils surrounding linked industrial units [103]. Superphosphate fertilizers have significant quantities of ^{210}Pb and ^{210}Po , which can provide these radionuclides to plants. Transfer factors for ^{137}Cs are two orders of magnitude lower in high-fertility soils than in low-fertility soils. As previously mentioned, potassium is the chemical counterpart of cesium, which is an alkaline element. Plant uptake of Cs decreases as soil potassium levels rise [104]. Illicit clay minerals can bind cesium ions strongly on frayed-edge regions, inhibiting plant absorption [105]. The main source of soil contamination is the naturally occurring isotope ^{40}K . Regardless of the location of the sample, it gives 60–65% of the total radioactivity. With 370 Bq/kg of soil, radioactive isotopes make up 0.0119% of the overall potassium content [106]. Several factors

impact radionuclide dispersion and absorption in vegetable plants, including crop type, fertilizer application, irrigation, plowing, liming, climatic conditions, organic matter content, and others [27, 107, 108]. Technologies employed in agricultural cultivation may alter the soil's physical characteristics or cause a redistribution of radioactive material in the root zone, which may have an impact on crop radionuclide accumulation [109]. For instance, uranium precipitation by soils is frequently low at pH values below 3, rises quickly from pH values of 3 to 5, peaks in the pH region of 5 to 7, and subsequently diminishes with rising pH values after reaching pH 7 [110, 111]. On the other hand, low levels of clay, organic matter, and high calcium concentrations in the soil solution or exchangeable phase can increase radium availability in the soil [28, 104]. Most of the researchers have detected ^{235}U , ^{232}Th , ^{226}Ra , and ^{40}K in soil and LPG, including their radiological impacts [113-126]. The radionuclides ^{90}Sr , ^{131}I , and ^{137}Cs in vegetables cultivated in soil have also been studied [127–131]. Soil-to-plant transfer factors (TFs) are essential for assessing the harm to the ecosystem that radioactivity in soil and crops causes [112].

2.7 RADIOACTIVE IMPACT ON HUMAN HEALTH AND ENVIRONMENT

A radioactive gas that is chemically inert is radon. In that instance, radon won't be oxidized or have its radioactivity or form altered by combustion. It will be expelled from the body without any direct health effects when it enters the body through inhalation. However, the radioactive decay products of radon, such as lead, bismuth, and polonium, which can linger in the lungs after inhalation, are what pose the greatest risk to human health [33]. About 310 mSv of terrestrial radionuclides have been deposited in the human body as a result of ingestion and absorption, with the same outcome for radionuclide concentration in tissue [23]. Several studies have revealed that crude oil is the source of the ^{238}U and ^{232}Th series radionuclides that accumulate in LP gas during refining. They are radioactive and can increase the risk of cancer. There are 10 LPG companies in Bangladesh where liquefied petroleum gas is refined and bottled [132]. So, Bangladesh is a country that not only refines but also bottling of LPG. On the other hand, LPG may be released during bottling and spread into the environment. These released gases can be mixed with aerosol particles and increase the concentration of radionuclides in the atmosphere. The effects of these radionuclides, which can build up in the bodies of LPG employees over time, are long-lasting. In that case, the worker at the LPG bottling plant is affected by different types of complex

diseases, such as cancer of the kidneys and lungs and acute myeloid leukemia through inhalation or ingestion of these radioactive liquefied petroleum gases during bottling.

Gebeyehu & Bayissa. calculated the EDI, THQ, HI, and TCR of As, Cd, Hg, and Ni for tomato and cabbage. The health index (HI) related to ingesting hazardous metals from both vegetables had HI values of 7.205 and 15.078, respectively, which were significantly greater than one. According to his research, the intake of cabbage and tomato products grown in the Mojo region poses a high health risk (both non-carcinogenic and carcinogenic) to the consumer [87]. When vegetables are ingested, The target hazard quotients (THQ) for As, Co, and Hg are higher than the threshold value, indicating a health concern for both adults and children, according to Ashraf et al. Additionally more than one are the HI values for eating tomatoes, cabbage, okra, and brinjal, which are 8.1975, 15.3077, 8.7312, and 10.2306, respectively. Due to probable health risks, he advised against using these vegetables in this situation [133]. The health risk index (HRI) and plant transfer factor (PTF) of these substances from soil to vegetables were computed by Sultana et al. Because of the negative impacts of ionizing radiation, she discovered greater transfer factor values for all elements, indicating the region is radiologically risky for the locals. People in industrial regions consumed the most Fe, Cr, Mn, Pb, Zn, and As through their vegetable diet, whereas Cd was higher in non-industrial areas than in industrial areas [134]. According to calculations by Gupta et al., the target hazard quotients of Cd, Mn, and Pb for fenugreek (2.161, 2.143, and 2.228, respectively) and spinach (3.697, 3.509, and 5.539, respectively) were both higher than unity, indicating a significant likelihood of non-carcinogenic health concerns if people regularly consume these foods To stop an excessive buildup in the food chain, she suggested routine monitoring of the soil, irrigation water, and plants [135]. Miller et al. evaluated two further exposure pathways: one was the consumption of infected meat from cattle and fowl, which drink dirty water, and another was the ingestion of contaminated wind-blown dust [136]. Using Pb isotopic compositions, Wang et al. estimated the binary mixing model, which revealed that 35–80% of the contamination of Pb and As in vegetables was caused by steel-making operations [25]. The radium equivalent activity, absorbed dose, and external and internal risks were assessed by Khan et al. His calculations put the range of soil's radium equivalent activity as 79.79-226.09 Bqkg⁻¹. The range of external and internal

hazards was 0.22-0.61 and 0.28-0.82 in soil. The range of absorbed energy was 38.27-105.95nGyh⁻¹ [137].

Shanthi et al. found that the daily internal dose from ingesting radionuclides through food is 4.92mSv/d, and the annual dose is 1.79mSv/y. The most often consumed radionuclides are ⁴⁰K [138]. In order to determine the radiological risks, Aswood et al. calculated the annual effective dosage. The average effective dosage per year was determined to be 213.27Svy⁻¹ [139]. Pietrzak-Flies et al. evaluated that the annual effective doses for the ingested radionuclides from vegetables were 5.95μSv, of which 72.4% came from ²²⁶Ra [140]. The annual effective dosage from ingesting vegetables and associated components that contain long-lived natural radionuclides was similarly estimated by Santos et al. to be 14.5 Sv [141].

CHAPTER III

METHODOLOGIES OF ASSESSMENT

3.1 INTRODUCTION

The radionuclides and trace elements in the crude oil, LPG, and soil where they were mixed are investigated using INAA (Instrumental Neutron Activation Analysis) and a gamma-ray HPGe detector. For the LPG energy management and safety of people and the environment, the study area, the specific goal of the study, the instrument, the INAA technique, the INAA irradiation procedure, the gamma-ray HPGe detector, and some mathematical modeling of the hazards are presented. Figure 1.11 provides the flowchart for the research process. The entire process is depicted by a flow chart in Figure 3.1 for the detection of radionuclides and traces of other hazardous materials in crude oil, LPG, and soil samples. Using ALOHA software, this study also evaluates fluid behavior following environmental exposure, the consequent emissions, potential injuries, and the safest radius for fire, explosion, and hazardous emissions. This outcome is used to generate appropriate risk assessment evaluations that can be made available to the industry in an effort to lessen the potential consequences of such events in the future. This study also analyzes the energy consumption related to safety issues and develops an equation for weight calculation that can be used by any LPG bottling plant company to ensure how much LPG is actually release into environment.

3.2 ANALYTICAL METHOD OF LPG HAZARDERS

The study is mainly concerned with the dangers posed by LPG emissions during bottling into cylinders. In this work, assuming a variable amount of LPG discharged into the environment, Areal Location of Hazardous Atmosphere (ALOHA) models have been utilized to assess the danger of fire and explosion from different LPG compounds. Another notable concern is the environmental impact of toxic gas emissions. ALOHA is the most powerful and widely used program to mimic the environmental response of substance release. A specific piece of computer software called ALOHA, which stands for "Areal Locations of Hazardous Atmospheres," helps us respond to inadvertent chemical leaks more effectively by anticipating and forecasting the leaking process. This software can forecast all of the consequences of chemical discharge, including flames and toxic substances in the environment. The

Environmental Protection Agency (EPA) created this program to model mishaps brought on by the release of explosive and hazardous substances. To reduce user mistakes, the application has a big database (data for over 1000 chemical compounds) and a simple working environment. Regardless of the gravity of the risk of chemical exposure, a crisis response plan must have been created [142]. ALOHA software is simple to use and requires few inputs. As a result, its assumptions occasionally diverge from real circumstances. However, the impact range is just about in the same range (+/- 10%), which is acceptable [142].

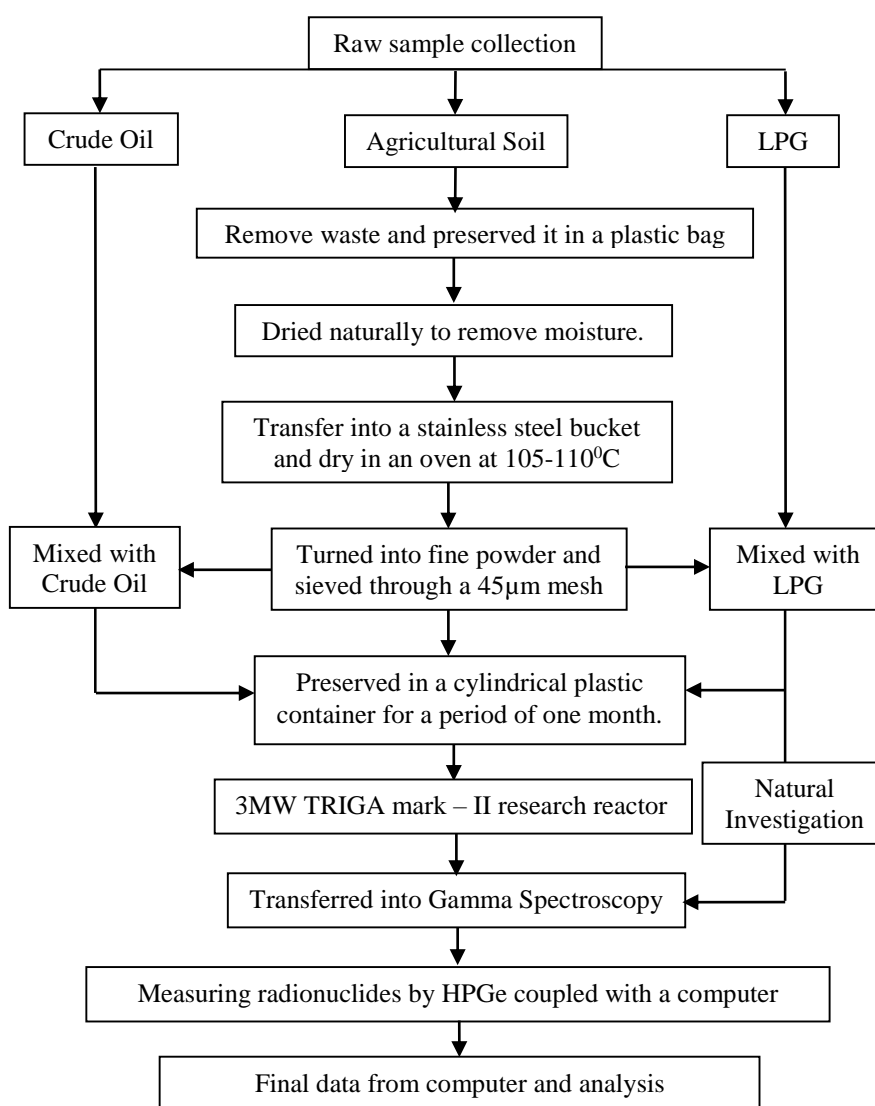


Figure 3.1: Flow Chart of the Data Preparation and Analysis

3.3 SOIL, CRUDE OIL AND LPG SAMPLE PREPARATION

3.3.1 Sample Preparation of Soil and LPG for Natural Irradiation

Five kilograms of soil samples were taken from the Raozan and Rangunia Upazilas'

agricultural land. Before drying, roots, stones, and other debris were taken out. Following that, soil samples were naturally dried for two to three days in eight hours in the sun to remove moisture. Soil samples were dried from February 10 to February 18, 2022, when the humidity ranged from 35 to 78% and the temperature ranged from 21 to 27°C. After naturally drying, the soil samples were dried in a “Forced Air Drying Oven” at 105°C for 8 hours at constant weight. All of the soil samples reached consistent weight after drying in the oven for 24 hours. An agate mortar and pestle were used to grind the dry soil samples. To preserve equal grain size, the ground soil samples were then sieved through a 45µm screen. Then the sample was weighed using a microbalance and sealed into a Teflon bag. The step of soil sample preparation is shown in Figure 3.2.



Figure 3.2: Steps of Soil Sample Preparation for Irradiation

The two samples of crude oil imported from Abu Dhabi and Saudi Arabia were collected (dates: 21.2.2022 and 15.5.2022) from the refineries of our country. The four samples of LPG imported at different dates (18.5.2022, 7.6.2022, 2.7.2022, and 28.8.2022) were collected from a local LPG bottling plant. The tested parameters of the collected LPG samples are given in the appendix (Table A.4). From ready-dried fine soil, three soil samples (ID No. S-1, S-2 and S-3) were prepared. Again the LPG collected at different dates was mixed with the dry soil and prepared into three another samples (ID Nos. LPS-1, LPS-2 and LPS-3). Then the samples were weighed using a microbalance and sealed into an assigned plastic pot, as shown in Table 3.1. and Figure 3.3

All prepared soil and LPG samples were preserved for one month in a dust free chamber for natural irradiation activation. Following the testing period, samples of soil and LPG that were ready for preservation were sent to a gamma spectrometer for analysis in order to identify any potentially dangerous naturally occurring radionuclides.

Table 3.1: Weight of the Soil and LPG Samples for Natural Irradiation

Sample ID	(P+S) (g)	P + S+L (g)	L (g)
LPS-1	310.92	324.25	1.12
LPS-2	310.88	326.32	4.01
LPS-3	311.02	331.62	7.82
Sample ID	P(g)	P +S (g)	S (g)
S-1	69.05	319.05	250
S-2	70.62	320.62	250
S-3	69.25	319.25	250



Figure 3.3 Soil and LPG Samples for Natural Irradiation

3.3.2. Sample preparation for INAA

Six samples—one soil sample (ID No. SL-1), five LPG samples (mixed with dirt) (ID Nos. LPG-1, LPS-2, LPS-3, LPS-4, and LPS-5) and two crude oil samples (crude oil was mixed in tracing paper, not with soil) were prepared for INAA testing. Tables 3.2 and 3.3 display the soil sample weights and Teflon bag usage. After being weighed, the sample package was put in another packet known as the cover packet. Finally, according to the sample ID, the cover packet was labeled with an identifying number. Then, the packets were carefully stored in preparation for neutron irradiation. About 50 mg of soil, 50 mg of LPG, and 70 mg of crude oil were utilized in this experiment.

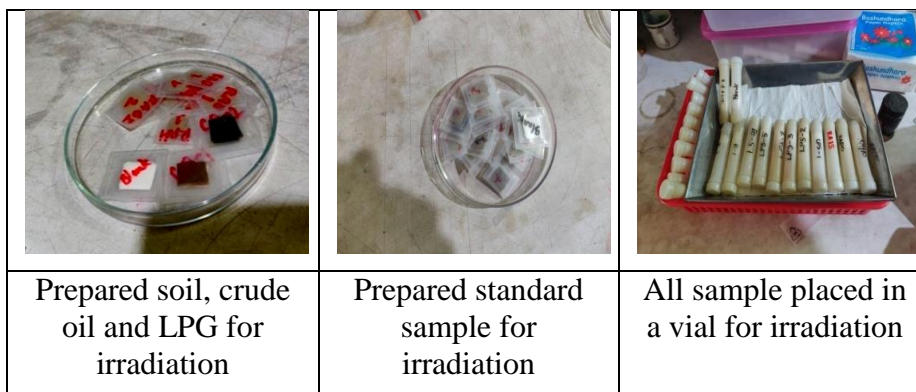
Three standard reference materials were employed in this study for the comparative standardization technique: IAEA-Soil-7, IAEA-SL-1, and NIST-1633b. IAEA-SL-1 (lake sediment; IAEA: International Atomic Energy Agency) and IAEA-Soil-7 were used as control samples to ensure the analytical quality of the results, whilst NIST-1633b (coal fly ash) was used as a standard. All of the standards were made in the same way that the samples were. Three standards, three foils, and the samples were put in a vial to be exposed to irradiation. Figure 3.4 shows the prepared sample for irradiation

Table 3.2: Weight of the Soil and LPG Mixed Soil Samples

Sample ID	PE bag (g)	PE + Sample (g)	Sample (g)
1633b	0.10405	0.15351	0.04946
Soil-7	0.11774	0.17017	0.05243
SL-1	0.11992	0.17349	0.05357
Blank			0.08306
R1	0.08173	0.10380	0.02207
R2	0.10148	0.21957	0.11809
LPS-1	0.10429	0.15598	0.05169
LPS-2	0.11167	0.16420	0.05253
LPS-3	0.07858	0.12979	0.05121
LPS-4	0.09216	0.14068	0.04852
LPS-5	0.08863	0.13937	0.05074
LS-1	0.13985	0.1244	0.05259
F-1			0.00354
F-2			0.00356
F-3			0.00167

Table 3.3: Weight of the Crude Oil (mixed with trace) Paper Samples

Sample ID	PE bag (g)	PE + Sample (g)	Sample (g)
CO-1	0.15234	0.22533	0.07299
CO-2	24.79957	24.87163	0.07206
Soil-7	0.10695	0.15972	0.05277
SL-1	0.11992	0.17349	0.05357
Blank			14.12994
B			0.09548
F-1			0.00354
F-2			0.00356
F-3			0.00167

**Figure 3.4: Prepared Soil, Crude Oil, and LPG Samples for Irradiation**

3.3.3 Irradiation by Research Reactor (3MW TRIGA Mark-II)

Using a pneumatic transfer (rabbit) system, two irradiation procedures were completed at the 3MW TRIGA Mark-II research reactors in the Bangladesh Atomic Energy Commission, Savar. (i) All samples and standards underwent simultaneous long irradiation for 1.47 hours at 250 kW with a thermal neutron flux of $2.11 \times 10^{13} \text{ n.cm}^{-2}\text{s}^{-1}$ (ii) Each sample underwent a short irradiation with a thermal neutron flux of $5.28 \times 10^{12} \text{ n.cm}^{-2}\text{s}^{-1}$ for 1 minute at 250 kW. To measure the neutron flux gradient inside the sample stack, three IRMM-530RAAl-0.1% Au (0.1 mm foil) monitor foils were positioned at the bottom, middle, and top of the stack and subjected to radiation for the extended irradiation method. The sample was irradiated in a 3 MW TRIGA Mark II research reactor at BAEC Savar in Dhaka, as shown in Figure 3.5.



Figure 3.5: BAEC Savar, Dhaka, 3MW TRIGA Mark-II Research Reactor

3.3.4. Gamma-ray Counting

Using a digital gamma-spectrometer (DSPEC JrTM, ORTEC) connected to a high-purity germanium detector (HPGe, CANBERRA, 1.8 keV resolution at 1332.5 keV of ^{60}Co , and 40% relative efficiency), samples were counted after being exposed to radiation. Figure 3.6 shows the HPGe detector at BAEC Saver, Dhaka, where the gamma-rays of the irradiated sample was counted.

For short irradiation, the first counting was carried out for 300s following a decay time of around 300s, and the second counting was carried out for 250–300s following a decay time of 2-3 h. Two counts were made for samples exposed to long-irradiation: after a decay time of 1-2 days, for 1200 seconds, and then after a decay time of 7-10 days, for 7200 seconds. Heavy metals with short and long half-lives were identified independently from those with short and long irradiation. A PC-based HPGe detector

coupled with a digital gamma spectrometry system was used to conduct gamma spectrometric analysis on all irradiated samples and validated reference materials. Data was acquired using the programs Genie-2000 (Canberra) and MAESTRO-32 (ORTEC). The program Hypermet PC version 5.12 was used to carry out the gamma peak analysis. Figure 3.7 shows the gamma peak analysis of the irradiated sample.

As shown in Figure 3.8, the high-purity germanium detector at the Chittagong Atomic Energy Centre measures the naturally occurring radionuclides of LPG. For irradiated samples, counting was done for 20000 seconds after 4-week squalor equilibriums.



Figure 3.6: HPGe Detector at BAEC Savar, Dhaka

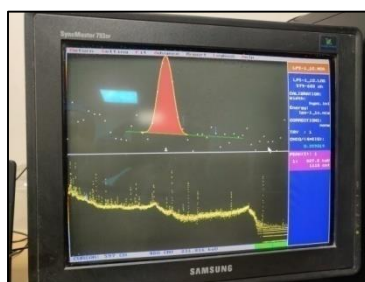


Figure 3.7: Analyzing the Gamma Peak with Hypermet PC Version 5.12.



Figure 3.8: HPGe Detector at Chittagong

There are three high-resolution gamma spectroscopy detectors at the NRL (Nuclear Reactor Laboratory) gamma spectroscopy facility in Chittagong. To identify and measure radioisotopes in samples, these high-purity germanium detectors (HPGe) all have copper-lined lead caves to reduce background. A GRSS detector channel typically consists of a high-purity germanium (HPGe) semiconductor detector, a pre-amplifier, an amplifier, a high-voltage power supply, a multi-channel analyzer (MCA), and a computer-based acquisition and analysis system. In current systems, a number of these parts are combined into integrated units. NRL use the Canberra Lynx system, which combines the power supply, digital amplifier, and MCA into a single box.

3.3.5. Fundamental Equations for the INAA Method

The rate of product growth in a reaction powered by neutrons depends on the magnitude of the neutron flow. With increasing neutron size, interaction rates rise. The associated INAA approach's mathematical calculations and theoretical underpinnings for the basic governing equations as in Eqn. (3.1) is followed:

$$A_o = \frac{\text{Net count rate}}{\varepsilon_\gamma \times I_\gamma} = \frac{\frac{\text{Counts}_{\text{sample}} - \text{Counts}_{\text{background}}}{\text{Counting time } (t_c \text{ in second})}}{\varepsilon_\gamma \times I_\gamma} \quad (3.1)$$

Equation 3.1 demonstrates how to compute the induced activity (by neutron irradiation) A (Bq) of an element using the net count rate, gamma detector counting efficiency (ε_γ), and gamma-ray emission probability (I_γ). In order to calculate the corrected induced specific activity (A in Bq.g-1) of an element, one must have the irradiated sample mass (m in g), the induced activity (A in Bq.g-1), the irradiation factor $(1 - e^{-\lambda t_i})$, the decay factor $(e^{-\lambda t_d})$, and the counting factor $(1 - e^{-\lambda t_c})$. The basic governing equations as in Eqn. (3.2) is followed:

$$A(\text{Bq}) = \frac{\text{Net count rate}}{\varepsilon_\gamma \times I_\gamma \times m} \times (1 - e^{-\lambda t_i}) \times (e^{-\lambda t_d}) \times \frac{(1 - e^{-\lambda t_c})}{\lambda t_c} \quad (3.2)$$

the decay constant (s^{-1}), the irradiation time (s), the decay time (s), and the counting time (s), respectively, are denoted by the letters, t_i , t_d , and t_c . Equation 3.3 can then be used to determine the elemental concentrations in the measured sample (C_{Sample}) based on the corrected induced specific activities of an element in the sample (A_{Sample}), in the standard (A_{Standard}), and elemental concentrations in standards C_{Standard} . The basic governing equations as in Eqn. (3.3) is followed:

$$C_{\text{Sample}} = \frac{A_{\text{Sample}}}{A_{\text{Standard}}} \times C_{\text{Standard}} \quad (3.3)$$

The mathematical terms like gamma-ray emission probability (I_γ), counting efficiency of the gamma detector (ϵ_γ), neutron flux of the reactor (Φ in neutrons.cm⁻²s⁻¹), nuclear activation cross-section (σ), fractional isotopic abundances of the targeted element ($F_{e,i}$), the element's atomic weight (M), and Avogadro's number (N_A : 6.023×10²³ atoms.mol⁻¹) are the same for both sample and standard in this relative standardization approach. Thus, these terms will be nullified when using Eq.3.3.

3.3.6 Radioactivity Conversion and Data Quality:

The correctness of the results has been validated by triple measurements of SL-1 and Soil-7 (n = 3). After taking into account a number of analytical mistakes, the measured abundances of elements in reference materials were equivalent to certificate values. For the measured abundance elements in SL-1 and Soil-7, this study's reproducibility (RSDs in%) ranged from 4.1 to 8.8%. Using the Eq.3.4 (Abedin & Khan), the relevant specific activity (Bq.kg⁻¹) was calculated from the respective elemental abundances of U (µg. g⁻¹), Th (µg. g⁻¹), and K (%). The basic governing equations as in Eqn. (3.4) is followed:

$$A_n = \frac{\lambda_{E,n} \times N_A \times f_{E,n}}{M_E \times k} \times C_E \quad (3.4)$$

Where A_n is the measured radioactivity concentration of radionuclides n in Bqkg⁻¹; $\lambda_{E,n}$ is the decay constant of the radionuclides n of element E (s⁻¹); N_A is the Avogadro's number, $f_{E,n}$ is the natural abundance of radionuclides n of element E, M_E is the atomic mass (kg.mol⁻¹); C_E is the detected elemental concentration (µg.g⁻¹ or %); and k is the constant value (1000000 for U and Th concentration in µg.g⁻¹ or 100 for K in % of mass fraction)

The detected elemental concentrations of uranium (in µg. g⁻¹), thorium (in µg. g⁻¹), and potassium (in%) in vegetables can be converted into the radioactive concentrations of ²³⁸U, ²³²Th, and ⁴⁰K (in Bq.kg⁻¹). using the IAEA's suggested conversion factors. According to Abedin & Khan, these are 1%K = 313 Bq.kg⁻¹ ⁴⁰K; 1µg.g⁻¹ Th = 4.06 Bq.kg⁻¹ ²³²Th and 1µg.g⁻¹ U = 12.35 Bq.kg⁻¹ ²³⁸U.

3.3.7 Accuracy and Precision

In elemental analysis, accuracy and precision are the two crucial words. Each analysis carefully calculates it. Data becomes erroneous and imprecise as a result of a small error that creates a significant disturbance. Accuracy is also being used to assess statistical bias and describe systemic errors. The degree to which measurements of a quantity are

made in close proximity to that number's actual value is how we might characterize the accuracy of a measuring system in the domains of science, engineering, and statistics.

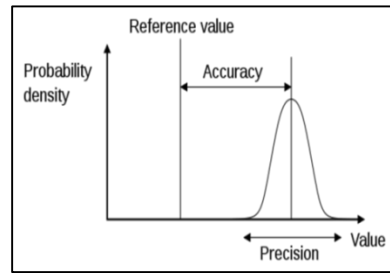


Figure 3.9: Presentation of Accuracy and Precision Graphically [143]

The consistency with which results are produced by repeated measurements under the same conditions is referred to as a measuring system's accuracy, which is related to reproducibility and repeatability. According to ISO 5725-1, accuracy is made up of truth and precision. Repeatability is the variation that happens when conditions are kept as constant as feasible by using the same instrument and operator and repeating within a short period of time. Repeatability is the variation that occurs when the same measuring technique is applied over a prolonged period of time with different instruments and operators. Figure 3.9 displays the accuracy and precision data graphically [143].

CHAPTER IV

RESULT AND DISCUSSION

4.1 LPG WEIGHT LOSS IN STORAGE TANKS OF BOTTOLING PLANT

During bottling of natural gas, the basic governing equations as in Eqn. (4.1) and Eqn. (4.2) are followed:

$$\text{Observed pressure, } P = P_g + P_{at} \quad (4.1)$$

Where P_g = Gauge pressure and P_{at} = Atmospheric pressure

Gas law equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (4.2)$$

Where, P_1 = observed tank pressure, V_1 =volume of the vapor of LPG in the tank, T_1 = Storing temperature. According to NTP condition, $P_2=1.01325\text{kg/cm}^2$ and $T_2=20^\circ\text{C}$ or 293°K . V_2 = volume of vapor at NTP. Specific weight of LPG liquid ($\text{Sp.wt}_{\text{LPG}}$) at 15.56°C is 0.52.

4.1.1 Weight of the volumetric quantity of LPG in the spherical storage tank

Generally, the weight loss of LPG in the tank is occurred following the Eqn. (4.3).

$$\text{Weight of LPG Liquid in the tank} = \text{Sp.wt}_{\text{LPG}} \times \text{Vol. LPG Liquid (in the tank)} \quad (4.3)$$

Consider storage tank capacities are 50MT and volumes 106m^3 . Generally, LPG is stored in the tanks in liquid form. Before being burned, LPG is converted back to gas. As a result, the LPG cylinder is filled to 80% capacity, which is 80% liquid and 20% vapor [7]. In that case, the volumes of the LPG liquid and vapor are 84.8 m^3 and 21.2 m^3 respectively, as given in Table 4.1. Initial measurements of the LPG storage tanks are done using their spherical and cylindrical forms as well as their capability to store LPG at 25°C . The measurement of the spherical tanks is based on a volume that is equal to the mass of LPG stored plus an additional 10% factor [shown in Appendix-A4][18]. So assuming the temperature range for storage tanks is $25\text{-}29^\circ\text{C}$ ($298\text{-}302^\circ\text{K}$), as given in Table 4.1. When operating at 14.34 bar of pressure, the LPG pump fails because of a leak in the discharge line [20]. Table 4.2 lists the tank pressure range of 6 to 10 kgcm-2. Table 4.2 further details the weight loss that occurs when a storage tank is filled from a jetty or cargo ship while the pressure and temperature are fluctuating.

Table 4.1: Volume of LPG Liquid (80% of Tank Capacity) with Variable Temperature and Pressure

Tank Capacity (m ³)	Liquid (80%) (m ³)	Vapor (20%) V ₁ (m ³)	Tank observed pressure P ₁ Kg/cm ²	Tank storage temperature T ₁ (°K)	Vapor (NTP) V ₂ (m ³)
106	84.8	21.2	7.01325	298	144.27
			8.01325	299	164.29
			9.01325	300	184.18
			10.01325	301	203.93
			11.01325	302	223.56

Table 4.2: Weight Loss of LPG in Storage Tanks (Liquid 80% of Tank Capacity)

Tank capacity (MT)	Liquid (MT)	Vapor (NTP) V ₂ (m ³)	Vapor wt. (V ₂ /157) (MT)	Total Weight (MT)	Weight Loss (MT)
50	44.09	144.27	0.91	45	5.0
		164.29	1.04	45.13	4.87
		184.18	1.173	45.26	4.74
		203.93	1.29	45.38	4.62
		223.56	1.42	45.50	4.50

Figure 4.1 shows the total LPG weight in the storage tank with variable pressure. The total weight of the LPG is increasing with increasing tank pressure. Figures 4.1 and 4.2 show that the weight loss of LPG is decreasing with increasing tank pressure and temperature. But the tank pressure cannot exceed the 14.34 bar because of LPG pump fails due to a leak in the discharge line while storage operates at that pressure [20,21].

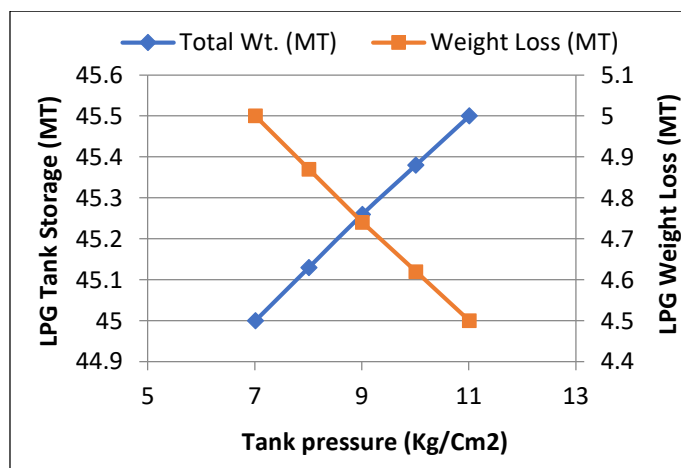


Figure 4.1: Total LPG Storage and Weight Loss with Variable Tank Pressure

This result suggests that the storage tank pressure and temperature can be considered as 10 kg/cm² and 30°C when filling the storage tank from the jetty. The LPG industry can follow this storage tank weight calculation for proper weight loss. The lost LP gas

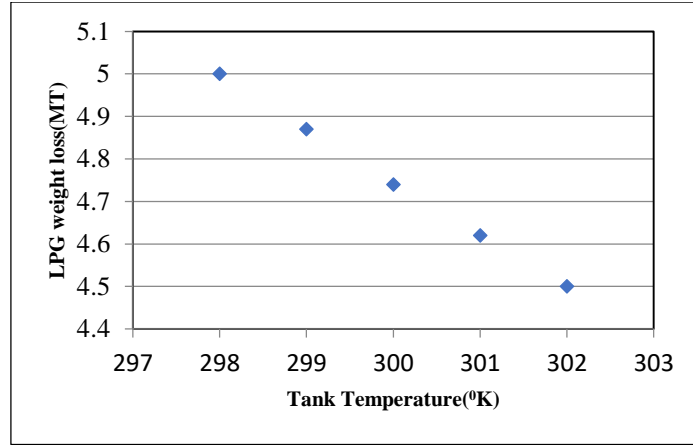


Figure 4.2: LPG Weight Loss in a Storage Tank with Variable Temperature

can spread into the environment, which may harm the environment, and human health. Safety is paramount in any industry, including the bottling process. Personal Protective Equipment (PPE) is used for worker safety. There is a considerable danger of leakage, hand and limb injury, noise pollution, fire, and other hazards. LPG leakage from the cylinder might occur during carousel filling. LPG leakage might also occur when unscrewing screws. While using the hoist-up cylinder on-line chain conveyor, hand and leg injuries are conceivable. The process of bottling can cause noise pollution.

4.2 EFFECT OF RELEASING LPG IN THE ENVIRONMENT WITH DIFFERENT WIND VELOCITY USING ALOHA

4.2.1. Governing equation

The discharge rate (kg/s) is calculated using the source model Eqn. 4.4, and the airborne concentration (ppm or mg/m³) is estimated using the dispersion model Eqn. 4.5. Finally, the fire and explosion models are employed to calculate thermal heat flow. Fluid mechanics formulas may be used to compute the liquid discharge rate from a storage tank [144]. The basic governing equations as in Eqn. (4.4) and Eqn. (4.5) are followed:

$$G_L = C_d A \rho_1 \left[\frac{2(p - p_a)}{\rho_1} + 2g \right]^{1/2} \quad (4.4)$$

where, G_L denotes the liquid mass emission rate (kg/s); C_d is the discharge coefficient (dimensionless); A denotes the discharge hole area (m²); ρ_1 =liquid density (kg/m³); p =liquid storage pressure (N/m² absolute); p_a =downstream (ambient) pressure (N/m² absolute); g =gravity acceleration (9.81 m/s²); H =liquid height above hole (m). The Gaussian Dispersion Model [144] can be used to compute the airborne concentration of a chemical due to dispersion from a continuous release source using the equation below

$$C(x, y, z) = \frac{G}{2\sigma_y\sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \left[\exp -\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2 + \exp -\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2 \right] \quad (4.5)$$

Where x, y , and z are the distances from the source, and m is the magnitude of the distance. (x denotes down wind, y denotes cross wind, and z is vertical) G = vapor emission rate (kg/s); H = height of source above ground level + plume rise (m); σ_y, σ_z = dispersion coefficients (m), function of distance downwind; u = wind velocity (m/s).

4.2.2. Flammable area of LPG vapor cloud with respect to wind velocity

For analyzing different hazardous areas, of the LPG bottling plant by using ALOHA software where chemical data of propane (C_3H_8), butane (C_4H_{10}), and isobutene (C_4H_8) are shown in Table 4.3. The least and upper acute levels of different LPGs in ALOHA are shown in Table 4.3. In this analysis, the wind velocity, environmental temperature and release time were remained constant. The wind velocity, environmental temperature, and releasing time 4.3 ms^{-1} , 31°C and 60 min respectively. This study mainly focused on the amount of LPG released how much effect the environment from its fire and flammable explosions from its vapor cloud. Several studies show that these releases LPG contain with different radioactive substances.

Table 4.3: Chemical Data for Different LPGs in ALOHA and Some Assumptions

LPG	AEGL-1 (60min) (ppm)	AEGL-2 (60min) (ppm)	AEGL-2 (60min) (ppm)	LEL (ppm)	UEL (ppm)	Assume LPG	
						Released (Kg/s)	Released Time (min)
Propane (C_3H_8)	5500	17000	33000	21000	95000	0.25	60
Butane (C_4H_{10})	5500	17000	53000	16000	84000	0.25	60
Isobutene (C_4H_8)	5500	17000	53000	18000	84000	0.25	60

In Bangladesh, the majority of LPG bottling plants employ a combination of 30% propane and 70% butane. We studied the danger zones of propane (C_3H_8), butane (C_4H_{10}), and isobutene (C_4H_8). Chemical data of different LPGs in ALOHA and some assumed data are given in Table 4.3.

Assuming a fixed amount of different LPG released into the surrounding environment in a certain period, as shown in Table 4.3. The values of AEGL-1, AEGL-2, and AEGL-3 for toxic area analysis are 5500, 17000, and 33000 ppm, respectively, assuming a release rate of 0.25 kg/s per LPG. The LEL concentrations of propane, butane and butadiene are 21000, 16000, 18000ppm respectively. For analyzing flammable vapor clouds ALOHA used 60% LEL for the red zone, 40% LEL for the orange zone, and

10% LEL for the yellow zone analysis.

The toxic area and flammable area of the vapor cloud for propane (C_3H_8) with variable wind velocity are shown in Table 4.4. For releasing 0.25kg/s of propane with variable wind velocity, the toxic area ranged from 11-30m. The red zone remains constant. The orange zone is ranged from 11 to 15m and the yellow zone is ranged from 25-30 m. Flammable areas of propane with variable wind velocity is ranged from 15-54 m. The red zone, orange zone and yellow zone vary from 18-19 m, 19-22 m and 49-54 m respectively.

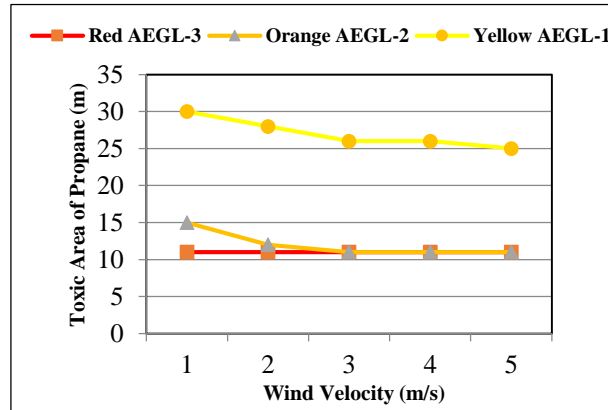
Table 4.4: Toxic and Flammable Area of Propane, Butane and Isobutene with Variable Wind Velocity

LPG	Wind Velocity (ms^{-1})	Toxic area(m)			Flammable area(m)		
		Red AEGL-3	Orange AEGL-2	Yellow AEGL-1	Red AEGL-3	Orange AEGL-2	Yellow AEGL-1
Propane (C_3H_8)	1.5	11	15	30	19	22	54
	2.5	11	12	28	17	20	49
	3.5	11	11	26	16	19	48
	4.5	11	11	26	16	19	49
	5.5	11	11	25	15	19	49
Butane (C_4H_{10})	1.5	10	17	33	23	28	64
	2.5	10	11	23	18	21	51
	3.5	10	11	22	16	20	49
	4.5	10	11	21	14	18	46
	5.5	10	11	21	14	18	45
Isobutene (C_4H_8)	1.5	10	17	33	22	26	60
	2.5	10	11	22	16	19	46
	3.5	10	11	22	13	18	44
	4.5	10	11	21	12	17	43
	5.5	10	11	21	12	16	43

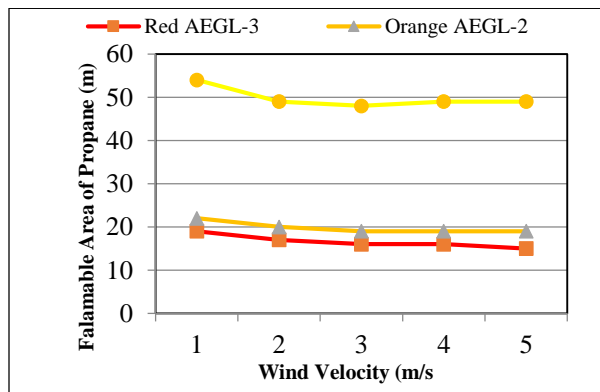
The toxic area and flammable area of a vapor cloud for butane (C_4H_{10}) with variable wind velocity are shown in Table 4.4. For releasing 0.25 kg/s butane with variable wind velocity, the toxic area ranged from 10-33 m. The red zone remains constant. The orange zone is ranges from 11-17m and yellow zone is ranged from 21-33 m. Flammable area of the butane with variable wind velocity is ranged from 14-64 m. The red zone, orange zone and the yellow zone are varying from 14-23 m, 18-28 m and 45-64 m respectively.

The toxic area and flammable area of the vapor cloud for isobutene (C_4H_8) with variable wind velocity are shown in Table 4.4. For releasing 0.25 kg/s isobutene with variable wind velocity, the toxic area ranged from 10-33 m. The red zone remains constant. The orange zone is ranged from 11-17m and yellow zone is ranged from 21-33 m. Flammable areas of isobutene with variable wind velocity is ranged from 12-60 m. The

red zone, orange zone, and the yellow zone vary from 12-22 m, 16-26 m and 43-60 m respectively. The flammability of the vapor cloud increases as the amount of LPG released increases. LPG vapor at concentrations ranging from 2% LEL to 10% LEL generates an explosive composite [145].



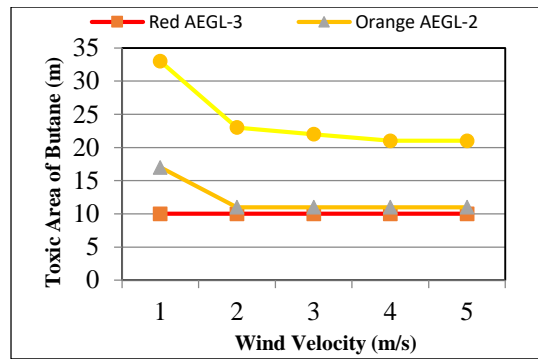
(a)



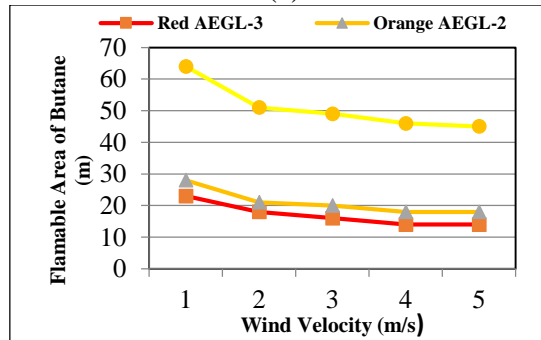
(b)

Figure 4.3: (a) Toxic and (b) Flammable Area of Propane with Wind Velocity

Figure 4.3(a) and 4.3(b) show that toxic and flammable areas of the propane are decreasing with increasing wind velocity. But the red zone of the toxic area remains constant. The hazardous and flammable regions of butane and isobutene are depicted in Figures 4.4(a) and 4.4(b) as well as Figures 4.5(a) and 4.5(b), respectively. Here also toxic and flammable areas are decreasing with increasing wind velocity. The red zone of the toxic area for all LPG propane (C_3H_8), butane (C_4H_{10}), and isobutene (C_4H_8) remains constant. The orange zone (AEGL-2) of all LP gas is a little bit decrease with increasing wind velocity. Figure 4.6 shows the comparison of toxic and flammable areas from vapor clouds of different LP gases.

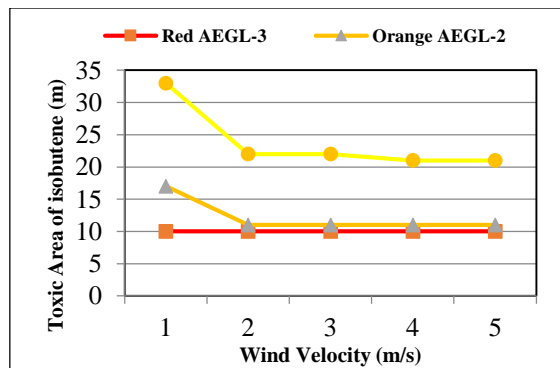


(a)

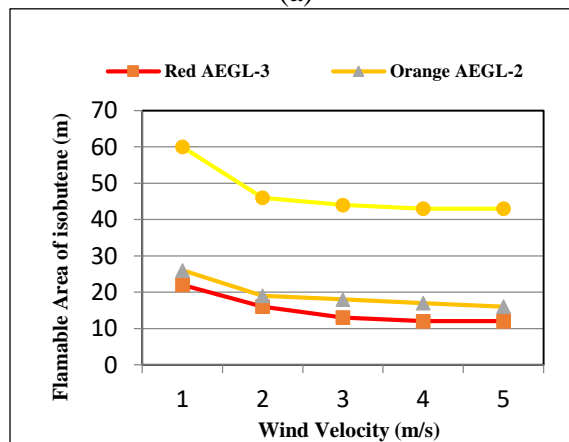


(b)

Figure 4.4: (a) Toxic and (b) Flammable Area of Butane with Wind Velocity



(a)



(b)

Figure 4.5: (a) Toxic and (b) Flammable Area of Isobutene with Wind Velocity

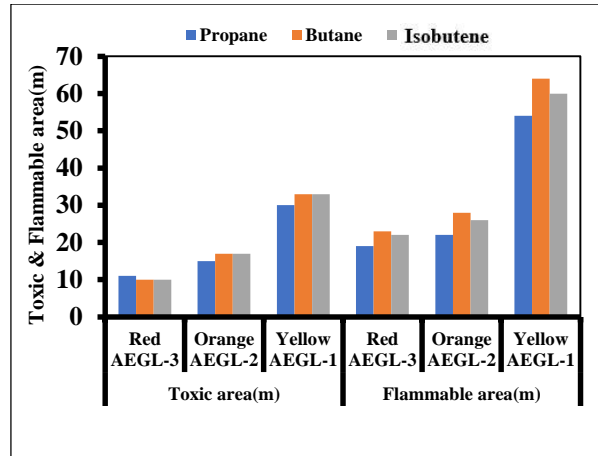


Figure 4.6: Toxic and Flammable Area of Release LPG

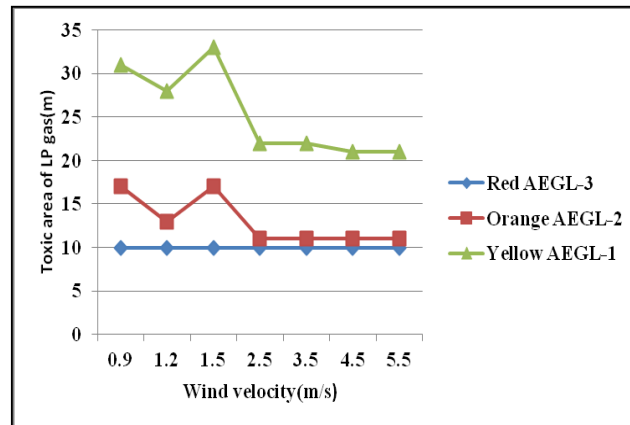


Figure 4.7: Toxic Area of LPG with Wind Velocity

The toxic and flammable areas of butane are higher than those of propane and isobutene. The red (AEGL-3) zone of toxic and flammable areas is propane > butane ≥ isobutene and butane > isobutene > propane. The orange (AEGL-2) zone of toxic and flammable areas is butane > isobutene > propane. The yellow (AEGL-1) zone of toxic and flammable areas is butane > isobutene > propane.

In ALOHA (version-5.4.7), input the minimum wind velocity can be 0.85 ms^{-1} . If we decrease wind velocity up to 0.9 ms^{-1} the red zone remains constant as shown in Figure 4.7. Yellow and orange zones decreased at 1.2 ms^{-1} , which is different from other cases.

4.3 ANALYZING THE FLAMMABLE AREA FROM RELEASING LPG DURING FILLING BOTTLE

The discharge rate (kg/s) is calculated using the source model Eqn. 4, and the airborne concentration (ppm or mg/m^3) is estimated using the dispersion model Eqn.5. Finally, the fire and explosion models are employed to calculate thermal heat flow. Fluid

mechanics formulas may be used to compute the liquid discharge rate from a storage tank [144].

For analyzing different hazardous areas of the LPG bottling plant by using ALOHA software, chemical data for propane (C_3H_8), butane (C_4H_{10}), and isobutene (C_4H_8) are shown in Table 4.5. The least and upper acute levels of different LPGs in ALOHA are shown in Table 4.6. In this analysis, the wind velocity, environmental temperature, and releasing time remained constant. The wind velocity, environmental temperature and releasing time were 4.3 ms^{-1} , 31°C and 60 min respectively.

Table 4.5: Chemical Data of Different LPGs in ALOHA

LPG	AEGL-1 (60min) (ppm)	AEGL-2 (60min) (ppm)	AEGL-2 (60min) (ppm)	LEL (ppm)	UEL (ppm)	Ambient Boiling Point ($^\circ\text{C}$)
Propane (C_3H_8)	5500	17000	33000	21000	95000	-42.2
Butane (C_4H_{10})	5500	17000	53000	16000	84000	-0.6
Isobutene (C_4H_8)	5500	17000	53000	18000	84000	-11.7

This study mainly focused on the amount of the LPG released and how much it affected the environment from its fire and flammable explosions from its vapor cloud. Several studies show that these releases LPG contain with different radioactive substances.

Table 4.6: Toxic and Flammable Area for Variable Amount of Releasing LPG with Constant Release Time (60 min) and Wind Velocity (4.3 m/s).

LPG	Amount release Kg/sec	Toxic area(m)			Flammable area(m)		
		Red AEGL-3	Orange AEGL-2	Yellow AEGL-1	Red AEGL-3	Orange AEGL-2	Yellow AEGL-1
Propane (C_3H_8)	0.25	11	11	27	16	21	49
	0.5	11	18	35	21	28	68
	1.0	15	23	49	29	38	94
Butane (C_4H_{10})	0.25	10	11	21	15	20	46
	0.5	10	13	29	21	26	63
	1.0	11	20	40	28	35	88
Isobutene (C_4H_8)	0.25	10	11	21	13	18	43
	0.5	10	13	29	19	23	59
	1.0	11	20	40	26	33	81

Most LPG bottling plants in Bangladesh use a mixture of 30% propane and 70% butane. In that case, we analyzed the threat zones of propane (C_3H_8), butane (C_4H_{10}), and isobutene (C_4H_8). Toxic area and flammable area of vapor cloud with different amounts of LPG release, such as propane (C_3H_8), butane (C_4H_{10}), and isobutene (C_4H_8) as shown

in Table 4.6. The values of AEGL-1, AEGL-2, and AEGL-3 for the toxic area analysis are 5500, 17000, and 33000 ppm, respectively. For releasing 0.25 kg/s propane, the red zone is 11m, the orange zone is 11 m and the yellow zone is 27 m. For releasing 0.25kg/s butane, the red zone is 10 m, the orange zone is 11 m and the yellow zone is 21 m.

Isobutene toxic zone shares the same hazard zone as butane. For releasing 0.5 kg/s propane, the red zone is 11 m, the orange zone is 18 m and the yellow zone is 35 m. For releasing 0.5 kg/s butane, the red zone is 10m, orange zone is 13 m and the yellow zone is 29m. The threat zone for toxic area of butadiene is same as butane. For releasing 0.1 kg/s propane, the red zone is 15 m, the orange zone is 23 m, and the yellow zone is 49 m.

For releasing 0.5 kg/s butane, the red zone is 11 m, the orange zone is 20 m, and the yellow zone is 40 m. Isobutene toxic zone shares the same hazard zone as butane's. From Table 4.6 it can be seen that the threat zone is increasing with the amount of LPG released. That's why the workers of the bottling plant can't be safe in that region with this amount of LPG release.

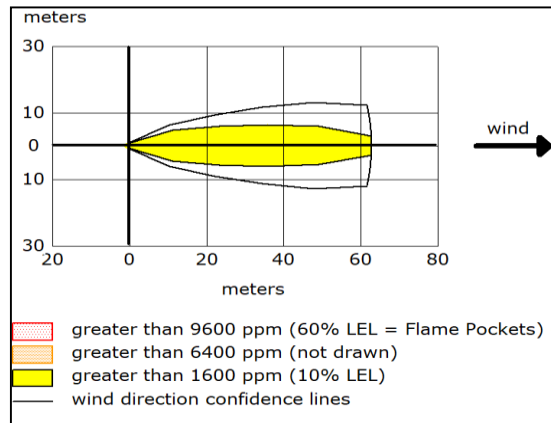
Flammable areas of LPG vapor cloud with respect to LPG released

The flammable areas of the vapor cloud for propane (C_3H_8), butane (C_4H_{10}), and isobutene (C_4H_8) are shown in the Fig. 4.8. The flammability of the vapor cloud increases as the amount of LPG released increases. LPG vapor at concentrations ranging from 2% LEL to 10% LEL generates an explosive composite [142].

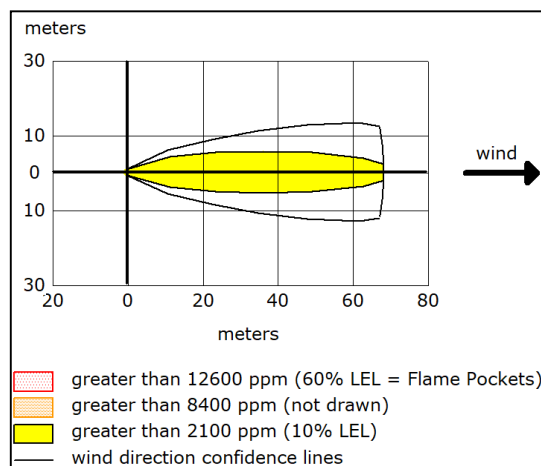
We can obtain the threat zone estimate for this situation from ALOHA. The yellow threat zone, according to ALOHA, extends 60 meters downwind from each LPG site. Ground-level LPG concentrations may be higher than the AEGL-1 limit in this zone. People may face major health problems or have trouble escaping at concentrations exceeding the AEGL-2 level. The LEL concentrations of propane, butane, and butadiene are 21000, 16000, and 18000 ppm respectively. For analyzing flammable vapor clouds ALOHA used 60% LEL for the red zone, 40% LEL for the orange zone and 10% LEL for the yellow zone analysis. The flammable area of vapor cloud for releasing 0.25 kg/s propane, the red, orange, and the yellow zone are 16, 21 and 49 m respectively. The flammable area of the vapor cloud for releasing 0.25 kg/s butane, the red, orange, and yellow zones are 15, 20, and 46m respectively.

The flammable area of vapor cloud for releasing 0.25 kg/s isobutene, the red, orange,

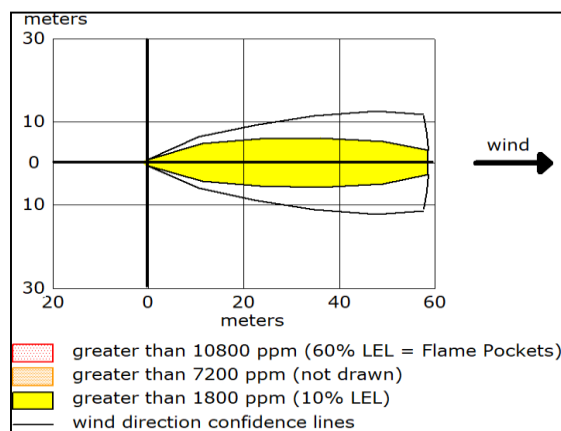
and yellow zones is 13, 18, and 43 m respectively. If increases the amount of released LP gas, the flammability is of the releasing gas also increases as shown in Figure 4.9. The blast wave created by the gas leak in the analyzed source is no bigger than 8 psi at any distance in the event of a vapor cloud explosion induced by an LPG gas leak [142].



(a)



(b)



(c)

Figure 4.8: Flammable Area of Vapor Cloud (a) Propane (b) Butane, and (c) Isobutene.

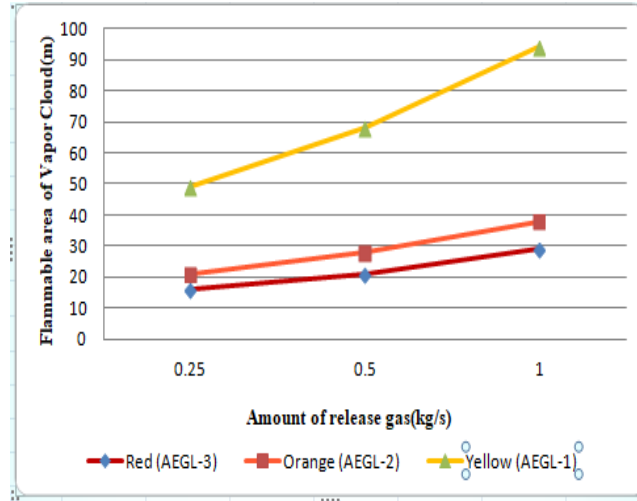


Figure 4.9: Flammable Area of Vapor Cloud with Variable Release LPG.

The flammable explosion of butadiene is less than the explosion of propane and butane, as shown in Figure. 4.10. In low-wind circumstances, the gas is expelled (immediately or constantly), forms a cloud, and disperses with an initial velocity. A fire and explosion risk assessment is necessary to apply the appropriate mitigation methods and emergency response protocols to protect employees [146].

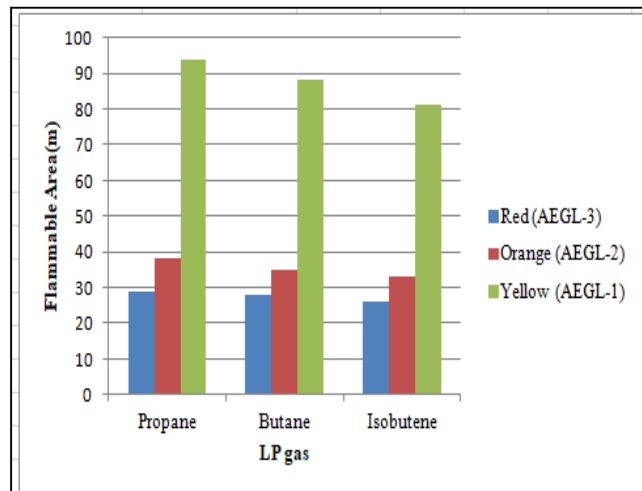


Figure 4.10: Flammable Area of Vapor Cloud of Different LP gas.

4.4.SAFETY ISSUE FOR WORKERS OF LPG BOTTLING PLANTS DUE TO RADIATION FROM LPG

The Eqn. (4.6) is used to estimate the airborne concentration of ^{222}Rn in a home or bottling plant due to radiation from LPG in an unvented appliance. Gesell et al. [68].

The basic governing equations as in Eqn. (4.6) is followed:

$$C_A = \frac{C_O \times Q \times DF}{V \times R} \quad (4.6)$$

Where C_A is the airborne concentration of ^{222}Rn (pCi/l), C_O is the concentration of ^{222}Rn (pCi/l) from LPG to home, Q is the quantity of LPG (m^3/day), DF is the decay factor due to storage in home tank (0.183 for 30 days), V is the house volume, and R is the air exchange rate (24 house volumes/day).

Among all radionuclides, gaseous radon can be exposed to land, air, plants, and water bodies, which causes lung cancer. The EPA reported that the average indoor radon level is about 1.3pCi/L while radon is found at about 0.4 pCi/L in the outside air [23].

Table-4.7 displays the radon concentration in each area of the LPG bottling factory. According to observations, the two areas of the LPG bottling facility with the highest radon concentrations are the Filling shed-2 and Sphere arc-2 sections, as shown in Table 4.7.

Table 4.7: Concentration of Radon (^{222}Rn) from LPG in Different Bottling Plant Sections

Different sections of the LPG plant	Radon (^{222}Rn) Concentration from LPG $\text{Bq/m}^3=0.27(\text{pCi/l})$ [C25,10][33,147]		Assume		Airborne concentration of $^{222}\text{Rn}/\text{month}$
			Room volume	LPG released	
	(Bq/m^3)	(pCi/l)	(m^3)	(m^3/day)	(pCi/l)
Empty shed-1	27.14	0.7334	440.26	360	0.137
Control room	23.36	0.63072	264.19	250	0.136
Filling shed-1	23.24	0.62748	435.2	210	0.069
Admin office	7.78	0.21006	300	50	0.008
Compressor shed	25.52	0.68904	120	320	0.420
Tank truck loading	24.85	0.67095	499.20	300	0.092
Sphere arc-1	26.58	0.71766	169.08	350	0.339
Fire station	29.54	0.79758	560.83	400	0.130
Filling Shed-2	43.72	1.18044	440.26	450	0.276
Sphere Arc-2	59.01	1.59327	155.29	530	1.243
Water treatment plant	9.80	0.26460	150	60	0.024

The concentration values of radon in the Filling Shed-2 and Sphere Arc-2 sections are 1.18 and 1.59 pCi/L which are higher than the EPA reported average indoor radon value of 1.3 pCi/L. Considering the volume of the room and quantity of LPG bottling or releasing, or refining in each section of the LPG bottling plant for determining the concentration of ^{222}Rn (pCi/l) in the atmosphere.

Due to the release of LP gas with radioactive radon, the concentration of ^{222}Rn is also increased in the atmosphere, as shown in Figure 4.11. The airborne concentrations of the empty shed, control room, filling shed-1, admin office, LPG compressor shed, tank truck loading, sphere arc-1, fire station, filling shed-2, sphere arc-2, and water treatment plant are 0.137, 0.136, 0.069, 0.008, 0.420, 0.092, 0.339, 0.130, 0.276, 1.243, and 0.024 pCi, respectively. But the concentration of ^{222}Rn in the sphere arc is 1.243(pCi/l) which is higher than the other section of the LPG bottling plant. It is not only depending on the quantity of LPG bottled or refined, or released but also on the volume of the room where the LP gas is released with gaseous ^{222}Rn . The variation of the concentration of ^{222}Rn released from the LP gas indifferent section of LPG plant is shown in the Figure 4.12. When LPG starts bottling, some pressure comes out of the container. Some liquid LPG is then boiled to produce steam. On the other hand, LPG expands rapidly as the temperature rises. So whenever a container is filled, there is enough space left for such expansion.

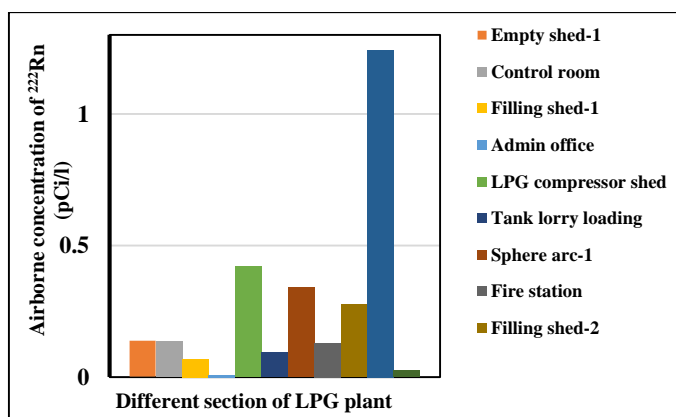


Figure 4.11: Variation of the airborne concentration of ^{222}Rn in Different LPG Plant Section.

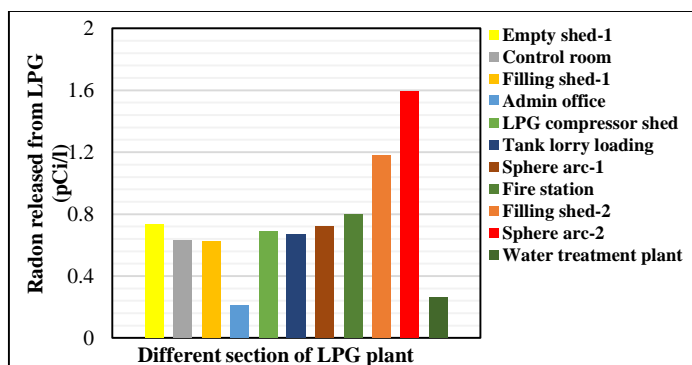


Figure 4.12: Concentration of ^{222}Rn Released from LPG per Month in Different LPG Plant Sections.

These steam releases during bottling depend on the operating pressure and temperature of the LP gas, as well as the nozzle and size of the container.

4.5. ELEMENTAL ABUNDANCE IN LPG MIXED SOIL AND LPG

In the LPG mixed soil, 25 different elements were identified and evaluated using INAA, including Na, Al, K, Sc, Mg, Cr, Mn, Fe, Co, Ce, Zn, V, As, Br, Rb, Sb, Cs, La, Sm, Eu, Yb, Hf, Ta, Th, and U. The accuracy of the results has been confirmed by triple measurements of SI-1 and Soil-7 ($n = 3$). The measured abundances of elements in reference materials were comparable with certificate values after considering a variety of analytical errors. The concentrations of the detected elemental abundance in the LPG mixed soil and the calculated elemental abundance in the LP gas are tabulated in Tables A.4 and A.5, respectively (see Appendix-A.4) as baseline data. We examine the origin of natural radionuclides (U, Th, and K) based on these results, as well as the effects of potentially harmful heavy metals (As, Cr, Co, Fe, Zn, and Mn) on the human body.

4.5.1. Concentration of radionuclides in a collected soil sample

The following formula (as in Eqn. 4.7) was used to convert the appropriate specific activity (Bq.kg^{-1}) from the respective elemental abundances of U ($\mu\text{g. g}^{-1}$), Th ($\mu\text{g. g}^{-1}$), and K (%). The basic governing equations as in Eqn. (4.7) is followed:

$$A_n = \frac{\lambda_{E,n} \times N_A \times f_{E,n}}{M_E \times k} \times C_E \quad (4.7)$$

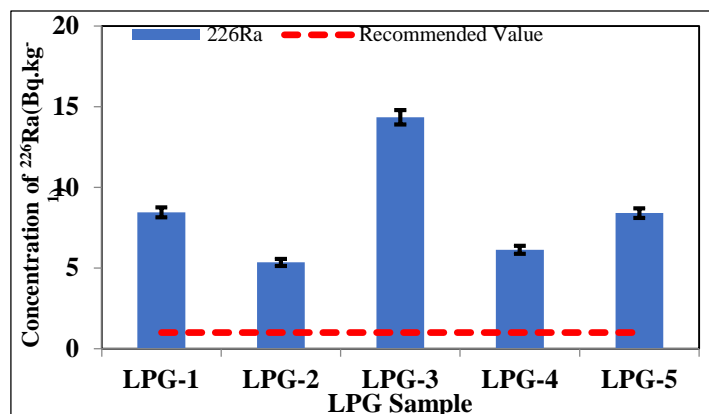
Where A_n is the measured radioactivity concentration of radionuclides n in Bq.kg^{-1} ; $\lambda_{E,n}$ is the decay constant of the radionuclides n of element E (s^{-1}), N_A is the Avogadro's number ($6.023 \times 10^{23} \text{ atoms.mol}^{-1}$), $f_{E,n}$ is the natural abundance of radionuclides n of element E , M_E is the atomic mass (kg.mol^{-1}).

Table 4.8: Radioactivity Concentrations in the LPG Samples Collected from the LPG Bottling Plant (INAA)

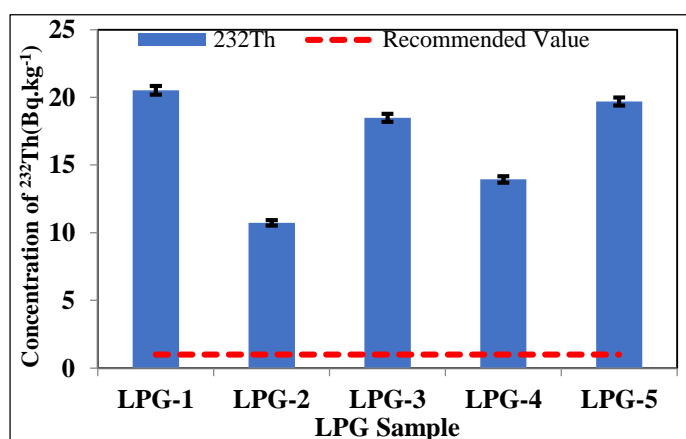
Sample ID	Radionuclides in LPG(Bq.kg^{-1})					
	^{226}Ra	\pm	^{232}Th	\pm	^{40}K	\pm
LPG-1	8.45	0.30	20.52	0.31	88.61	8.51
LPG-2	5.35	0.22	10.73	0.20	125.85	10.91
LPG-3	14.34	0.44	18.49	0.29	97.01	21.76
LPG-4	6.12	0.25	13.94	0.24	105.63	9.82
LPG-5	8.40	0.30	19.69	0.30	100.56	9.36
Mean($n=5$)	8.53		16.67		103.53	
Min.	5.35		10.73		88.61	

Max.	14.34	20.52	125.85
Guidance level	1 ^a	1 ^a	NG

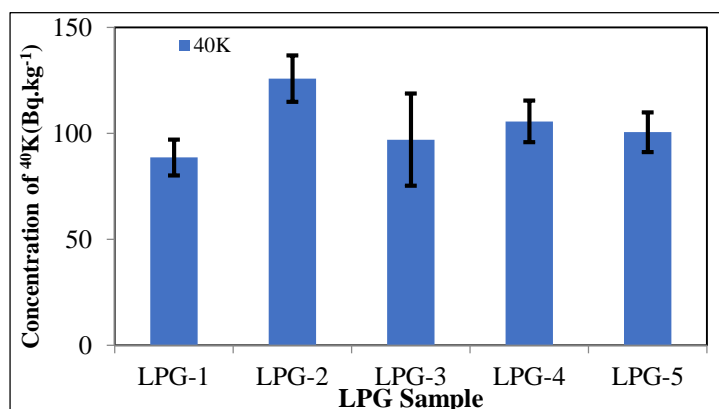
*NG=Not Given, ^a[162]



(a)



(b)



(c)

Figure 4.13: Concentration of (a) ^{226}Ra (b) ^{232}Th and (c) ^{40}K in LP Gas.

The IAEA-2003 (series TECDOC-1363) recommended conversion factors enables conversion of the measured elemental concentrations of uranium (in $\mu\text{g. g}^{-1}$), thorium (in $\mu\text{g.g}^{-1}$), and potassium (in%) in soil and LPG into the radioactive concentrations of ^{226}Ra , ^{232}Th , and ^{40}K (in Bq.kg^{-1}). These are $1\% \text{K} = 313 \text{ Bq.kg}^{-1} \text{ } ^{40}\text{K}$; $1\mu\text{g.g}^{-1} \text{ Th} = 4.06 \text{ Bq.kg}^{-1} \text{ } ^{232}\text{Th}$ and $1\mu\text{g.g}^{-1} \text{ U} = 12.35 \text{ Bq.kg}^{-1} \text{ } ^{226}\text{Ra}$.

The activity concentrations of radionuclides in LPG sample are listed in Table 4.8. The current study found that radionuclide concentrations in the LPG sample (Bqkg^{-1}) ranged from 5.35-14.34(^{226}Ra), 10.73-20.52(^{232}Th), and 88.61-125.85(^{40}K), with a mean value (n=5) of 8.53 (^{226}Ra), 16.67 (^{232}Th), and 103.53 (^{40}K).

The concentrations of ^{226}Ra , ^{232}Th and ^{40}K in LP gas are depicted in Figure 4.13. All of the collected LPG samples have ^{226}Ra and ^{232}Th values that are higher than the 1Bq.kg^{-1} WHO recommended threshold. The concentration of naturally occurring radionuclides in the LPG-mixed soil examined by the Chittagong Atomic Energy Commission is shown in Table 4.9. The activity concentrations of ^{226}Ra , ^{232}Th , ^{40}K and ^{137}Cs in LPG were determined to be 1.5–2.6, ND (not detected), 10–13, and ND (not detected), 1.7 Bq.kg^{-1} , respectively.

Table 4.9: Radioactivity Concentrations in the LPG Mixed Soil and LPG Samples

Radionuclides								
Sample ID	^{226}Ra (Bq.kg^{-1})	\pm	^{232}Th (Bq.kg^{-1})	\pm	^{40}K (Bq.kg^{-1})	\pm	^{137}Cs (Bq.kg^{-1})	\pm
LPS-1	19.8	2.574	12	3.6	184	23.92	1.7	0.476
LPS-2	18.8	2.256	22	5.06	187	26.18	1.4	0.42
LPS-3	16.2	1.944	10	1.8	153	24.48	ND	
S-1	17.6	1.936	22	4.62	171	23.94	ND	
S-2	16.2	1.944	12	3	160	24	1.5	0.6
S-3	14.7	1.764	8	1.6	49	24.5	1.4	0.42
LPG-1	2.2	0.638	ND	-	13	0.02	1.7	0.476
LPG-2	2.6	0.312	10	2.06	27	2.18	-	-
LPG-3	1.5	0.18	2	0.2	104	0.02	-	-
LPG-1=(LPS-1)-(S-1); LPG-2=(LPS-2)-(S-2); LPG-3=(LPS-3)-(S-3)								

*ND= Not detected

4.5.2. LPG might contain harmful metals

Table 4.10 lists the quantities of potentially hazardous elements in the LPG sample that was obtained. The levels of possibly harmful heavy metals in LPG (mgkg^{-1}) ranged from 0.70-1.66 (As), 1.7-2.78 (Co), 15.9-28.83 (Cr), 801.7-1299.6(Fe), 66.3-74.5 (Mn),

and 3.92-12.67 (Zn). The concentration of Cr is observed to be LPG-5>LPG-3>LPG-1>LPG-4>LPG-2. The concentration of Mn is observed to be LPG-2>LPG-5>LPG-1>LPG-3>LPG-2. The order of the LPG sample's Fe concentration is observed to be LPG-1>LPG-3>LPG-5>LPG-4>LPG-2.

Table 4.10: Potentially Toxic Metals in the LPG Samples Collected from the LPG Bottling Plant (INAA)

Element	Unit	LPG-1	±	LPG-2	±	LPG-3	±	LPG-4	±	LPG-5	±
Cr	mg/kg	25.9	0.59	15.9	0.43	27.8	0.62	21.43	0.54	28.83	0.64
Mn	mg/kg	66.3	1.13	74.5	1.24	66.12	14.30	69.	1.18	68.9	1.2
Fe	mg/kg	1299.6	16.98	801.7	12.43	1272.9	16.8	982.7	14.6	1161.4	16
Co	mg/kg	2.78	0.062	1.7	0.045	2.55	0.059	1.99	0.05	2.45	0.05
Zn	mg/kg	12.36	0.59	10.4	0.53	3.92	0.30	9.03	0.50	12.67	0.60
As	mg/kg	1.14	0.035	0.72	0.028	1.66	0.05	0.70	0.03	1.09	0.03

4.6. POTENTIAL RISK ASSESSMENT

The amount of ionizing radiation absorbed per unit mass of any material is known as the radiation dose. The absorption dose is the amount of energy that is concentrated in tissue as a result of exposure to ionizing radiation. While absorbed dose describes the energy deposit in a small tissue, equivalent dose discusses the consequences of radiation on a tissue. The overall amount of radiation received by the body's organs, the radiation's relative level of harm, and the radiation sensitivity of each organ are all taken into account when calculating the effective dose, which is stated in millisieverts (mSv).

Table 4.11: Calculated Radiological Risk Indices for the LPG Sample

Sample	REA (Bq.kg ⁻¹)	RLI (I _r)	H _{ex}	H _{in}	AD nGy/h	AED mSv/y	ELCR Sv ⁻¹
LPG-1	44.61	0.32	0.120	0.143	21	0.025	9.01×10 ⁻⁵
LPG-2	30.37	0.226	0.082	0.096	14.79	0.018	6.35×10 ⁻⁵
LPG-3	48.25	0.345	0.130	0.169	22.53	0.027	9.67×10 ⁻⁵
LPG-4	34.19	0.250	0.092	0.108	16.38	0.020	7.03×10 ⁻⁵
LPG-5	44.30	0.319	0.119	0.142	20.94	0.025	8.99×10 ⁻⁵
Mean(n=5)	40.344	0.292	0.1086	0.1316	19.128	0.023	8.21×10 ⁻⁵
Recommended Value*	370 ^b	<1 ^a	<1 ^a	<1 ^a	55 ^a	0.7 ^a	^a 2.90×10 ⁻⁴

* Representative level index (Raeq), Radium equivalent activity External, internal, and absorption dosages of hazards are listed; Annual Effective Dose = AED Excess Lifetime Cancer Risk (ELCR); UNSCEAR; Beretka & Mathew (2000)

Radium equivalent activity concentration

The total radium content of a sample is usually determined using the radium equivalent activity concentration (Req). Req is calculated under the presumption that the gamma dose rates for 10 Bq/kg of ^{226}Ra , 7 Bq/kg of ^{232}Th , and 130 Bq/kg of ^{40}K are equal. The basic governing equations as in Eqn. (4.8) is followed:

$$R_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_k \quad (4.8)$$

Where A_{Ra} , A_{Th} and A_k are the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K respectively.

Table 4.11 lists the computed radium equivalent activity. The LPG sample's radium equivalent activity ranges from 30.37- 48.25 Bq.kg⁻¹, with a mean value (n=5) of 40.34 Bq.kg⁻¹. The change of radium equivalent activity in the LPG sample is depicted in Figure 4.14. The acquired sample's radium equivalent activity is less than the advised level of 370 Bq.kg⁻¹.

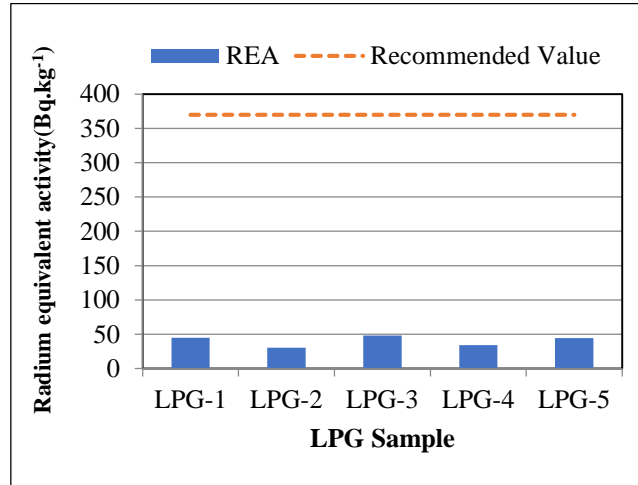


Figure 4.14: Changes in the Radium Equivalent Activity of an LPG Sample
Hazard Indices

Calculate the internal hazard index for the concentrations ^{226}Ra , ^{232}Th , and ^{40}K in gamma-ray specific activity. The basic governing equations as in Eqn. (4.9) is followed:

$$H_{in} = \frac{A_{Ra}}{185\text{Bq/kg}} + \frac{A_{Th}}{259\text{Bq/kg}} + \frac{A_k}{4810\text{Bq/kg}} \quad (4.9)$$

Where H_{in} is the internal index, A_{Ra} , A_{Th} and A_k are the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K respectively.

The external hazard index is a statement that quantifies the exposure factor and estimates the risk of natural gamma radiation from the terrestrial radionuclides ^{226}Ra , ^{232}Th , and ^{40}K . The basic governing equations as in Eqn. (4.10) is followed:

$$H_{\text{ex}} = \frac{A_{\text{Ra}}}{370\text{Bq/kg}} + \frac{A_{\text{Th}}}{259\text{Bq/kg}} + \frac{A_{\text{K}}}{4810\text{Bq/kg}} \quad (4.10)$$

Where H_{ex} is the external index, A_{Ra} , A_{Th} and A_{K} are the activity concentrations of ^{226}Ra , ^{232}Th , and ^{40}K respectively.

The representative level index can be used to calculate the radiation risk associated with terrestrial radionuclides using the basic governing equations as in Eqn. (4.11) is followed:

$$I_{\text{yr}} = \frac{A_{\text{Ra}}}{150\text{Bq/kg}} + \frac{A_{\text{Th}}}{100\text{Bq/kg}} + \frac{A_{\text{K}}}{1500\text{Bq/kg}} \quad (4.11)$$

Where I_{yr} is the representative level index, A_{Ra} , A_{Th} , and A_{K} are the activity concentration of ^{226}Ra , ^{232}Th and ^{40}K respectively.

The estimated levels of internal and external dangers are listed in Table 4.11 together with the representative level index. Internal, external, and representative level hazard index values for the soil sample range from 0.096-0.169, 0.082-0.130, and 0.226-0.345, respectively, with mean (n=5) values of 0.1316, 0.108, and 0.292. The variance of internal and external hazards as well as the representative level index of the LPG sample are shown in Figure 4.15. The investigated LPG's internal hazards, external hazards, and representational level index are all below the advised value of unity.

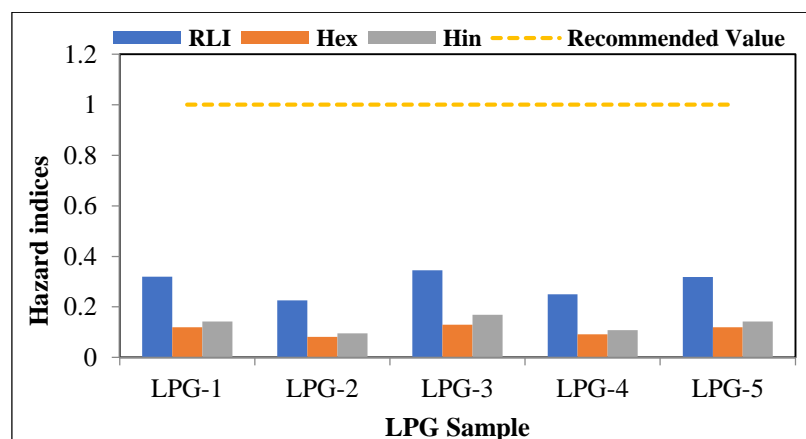


Figure 4.15: Changes in the LPG Sample's Representative Level Index, External Hazard, and Internal Hazard

Absorbed dose rate

In order to determine a characteristic of the external terrestrial gamma radiation, the absorbed dose rate was calculated in the air 1 m above the ground using the formula below. The basic governing equations as in Eqn. (4.12) is followed

$$D = [0.462A_{Ra} + 0.604A_{Th} + 0.0417A_k] \times (nGy/h) \quad (4.12)$$

Where D is the absorbed dose in air, A_{Ra} , A_{Th} , and A_k are the average activity concentrations of ^{226}Ra , ^{232}Th , and ^{40}K , respectively.

The calculated absorbed dose (AD) is tabulated in Table 4.11. The absorbed dose in the LPG sample ranged from 14.79-22.53 nGy.h⁻¹ with a mean (n=5) value of 19.12 nGy.h⁻¹. Figure 4.16 shows the variation of the absorbed dose of the studied LPG sample. The absorbed dose of the collected sample is less than the recommended value of 55nGy.h⁻¹

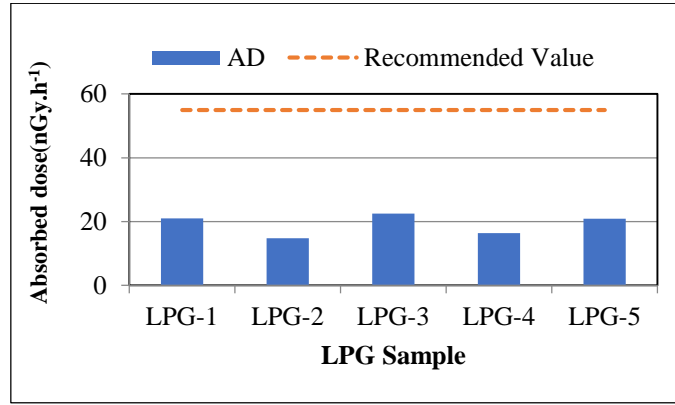


Figure 4.16: Variation of Absorbed Dose of the LPG Sample
Effective Dosage Rate Yearly

It is necessary to take into account both the outdoor occupancy factor and the conversion factor from the airborne dosage to the annual effective dose. The effective dosage received by adults was calculated using a conversion factor of 0.7SvGy⁻¹. The outdoor occupancy factor of 0.2 indicates that, globally, people spend 20% of their time outside. The annual effective dose was determined using the basic governing equations as in Eqn. (4.13) is followed:

$$D_{eff} = c \times D \times t \times P_{out} \times 10^{-6} \quad (4.13)$$

For adults with outdoor occupancy factors P_{out} , where D_{eff} is the annual effective dose, D is the absorbed dose, t is the yearly exposure period (8760), and c is the coefficient from the absorbed doses to effective doses.

Table 4.11 lists the determined annual effective dosage (AED). In the LPG sample, the annual effective dosage ranges from 0.018 to 0.027 mSv.y⁻¹, with a mean (n=5) value

of 0.23 mSv.y^{-1} . The variation of the annual effective dose for the LPG sample under study is depicted in Figure 4.17. The studied sample's absorbed dose is less than the suggested level of 0.7 mSv.y^{-1} .

Excess life time cancer risk is calculated by the basic governing equations as in Eqn. (4.14) is followed:

$$ELCR = D_{eff} \times A_{lf} \times R_f \quad (4.14)$$

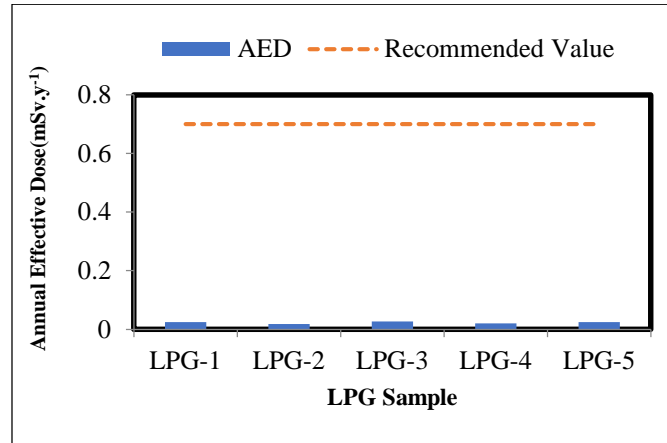


Figure 4.17: Changes in the Soil's Annual Effective Dose with Sampling Point
Excess Lifetime Cancer Risk

Where D_{eff} is the effective dose, A_{lf} is the duration of life (70 years) and R_f is the nominal co-efficient for determining the adjusted probability cancer risk of $0.5 \times 10^{-4} \text{ Sv}^{-1}$ for the whole population [117].

Table 4.11 lists the estimated excess lifetime cancer risk (ELCR) associated with breathing in contaminated LPG samples. The excess lifetime cancer risk for the LPG sample ranged from 6.35×10^{-5} – $9.67 \times 10^{-5} \text{ Sv}^{-1}$ with a mean ($n=5$) value of $8.21 \times 10^{-5} \text{ Sv}^{-1}$. Figure 4.18 shows the variation in excess lifetime cancer risk of the studied LPG sample, which is lower than the UNSCEAR-reported recommended value of $2.9 \times 10^{-4} \text{ Sv}^{-1}$.

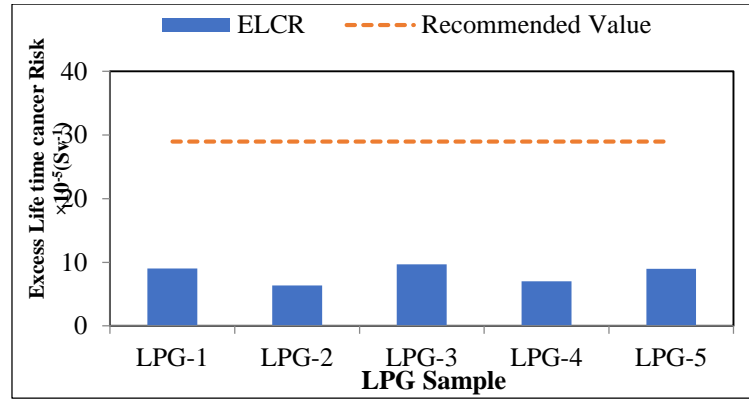


Figure 4.18: Variation of Excess Lifetime Cancer Risk of the LPG Samples.

The estimated excess lifetime cancer risk (ELCR) linked to breathing in polluted LPG samples is shown in Table 4.11. For the LPG sample, the excess lifetime cancer risk varied from 6.35×10^{-5} – $9.67 \times 10^{-5} \text{ Sv}^{-1}$, with a mean ($n=5$) value of $8.21 \times 10^{-5} \text{ Sv}^{-1}$. Figure 4.18 depicts the range in extra lifetime cancer risk for the LPG sample under study, which is less than the $2.9 \times 10^{-4} \text{ Sv}^{-1}$ UNSCEAR-reported recommended value.

4.7. HEAVY METALS RELATED HEALTH RISKS

The potential health effects of inhaling metal from LPG were examined using the hazard quotient and daily chronic inhalation. The daily chronic intake (CDI) was calculated for LPG using analysis of toxic metals, the basic governing equations as in Eqn. (4.15) is followed:

$$CDI_{\text{inhalation}} = \frac{EF \times ED \times IR \times C_i}{AT \times B_w \times PEF} \quad (4.15)$$

The Hazard Index (HI), which is based on the USEPA's health risk evaluation of chemical combinations, has been developed to evaluate all potential non-cancer impacts from multiple heavy metals. The Hazard Index (HI) was calculated for LPG using the basic governing equations as in Eqn. (4.16) is followed:

$$HI = \sum_i^n \frac{CDI}{R_{fd}} \quad (4.16)$$

R_{fd} stands for reference dose ($\text{mg kg}^{-1} \text{ day}^{-1}$). R_{fd} values are 0.3 for Zn, 0.0003 for Co, 0.024 for Mn, 0.7 for Fe, 0.0003 for As, and 0.003 for Cr (mg/kg/day), respectively. The constant variables of the equation are tabulated in Table 4.12.

Table 4.12: Constant Variables of the Equation

Parameter	Unit	Symbol	Value	References
-----------	------	--------	-------	------------

Exposure frequency	day.y ⁻¹	EF	180	[148],[149]
Exposure duration during ages	year	ED	30	
Average body weight during ages	Kg	Bw	70	
Average duration for no carcinogenic effects	(ED×365) day	AT	10950	
Inhalation rate	m ³ day ⁻¹	IR(inhale)	20	
Particle emission factors	m ³ kg ⁻¹	PEF	1.36×10 ⁹	[149]

The calculated daily inhalation toxic metals of the adult's people due to the inhalation of contaminated LPG is tabulated in Table 4.13. The average daily inhalations of As, Co, Cr, Fe, Mn, and Zn from LPG are 1.10×10^{-10} , 2.38×10^{-10} , 2.4×10^{-9} , 1.14×10^{-7} , 7.14×10^{-9} and 1×10^{-9} mg/kg/day.

The total number of metal risks is expressed by HI. The metals under consideration have no discernible effects on health if the $HI < 1$. If $HI > 1.0$, however, it suggests

Table 4.13: Calculated Daily Inhalation of Toxic Metals for the Adult Population due to the Inhalation of Contaminated LPG Samples

Sample	Cr	Mn	Fe	Co	Zn	As	HI
LPG-1	2.68×10^{-9}	6.87×10^{-9}	1.35×10^{-7}	2.89×10^{-10}	1.28×10^{-9}	1.19×10^{-10}	2.70×10^{-6}
LPG-2	2×10^{-9}	8×10^{-9}	8.00×10^{-8}	2×10^{-10}	1×10^{-9}	7×10^{-11}	2×10^{-6}
LPG-3	3×10^{-9}	7×10^{-9}	1×10^{-7}	3×10^{-10}	4×10^{-9}	2×10^{-10}	3.0×10^{-6}
LPG-4	2.20×10^{-9}	7.10×10^{-9}	1×10^{-7}	2.10×10^{-10}	9.40×10^{-10}	7.30×10^{-11}	2×10^{-6}
LPG-5	3×10^{-9}	7×10^{-9}	1×10^{-7}	3×10^{-10}	1×10^{-9}	1×10^{-10}	3×10^{-6}
Mean (n=5)	2.4×10^{-9}	7.14×10^{-9}	1.14×10^{-7}	2.38×10^{-10}	1×10^{-9}	1.10×10^{-10}	2.45×10^{-6}

potential health consequences. For $HI > 10.0$, a significant negative influence on chronic health has been proposed [35]. In that case, the hazard indexes (HI) from the LPG sample are less than one, indicating no health risk to human health for these metals.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

We have observed that the threat zone increase with decrease wind velocity. In cases of toxicity, the explosion tendency of LP gas varies in the order of butane>isobutene>propane, it indicates butane is more flammable than isobutene and propane.

In this research, we have analysed the threat zone of an LPG bottling plant with different amounts of LPG release using ALOHA software by point/area modelling. Here we have observed that the threat zone increases with increase LPG release, propane is more hazardous than butane and isobutene.

From the results and discussion on the impact of radionuclides in liquefied petroleum gas, the following conclusion can be drawn:

1. The concentration values of radon in the Filling Shed-2 and Sphere arc-2 sections are 1.18 and 1.59 pCi/L which are higher than the EPA reported average indoor radon value 1.3pCi/L.
2. The concentration of ^{222}Rn in the sphere arc is 1.243(pCi/l) which is higher than the other section of the LPG bottling plant.

Workers of the LPG bottling plant and the people of the nearby area can inhale these radioactive particles. In that case, they are affected by various complex diseases if they can't wear a mask or use other safety apparatuses to prevent these radionuclides.

The current research found that radionuclide concentrations in the LPG sample (Bqkg^{-1}) ranged from 5.35-14.34(^{226}Ra),

10.73-20.52(^{232}Th), and 88.61-125.85(^{40}K). The concentrations of potentially toxic heavy metals in LPG (mgkg^{-1}) ranged from 0.70-1.66 (As), 1.7-2.78 (Co), 15.9-28.83 (Cr), 801.7-1299.6(Fe), 66.3-74.5 (Mn), and 3.92-12.67 (Zn).

The average ($n=5$) values of radium equivalent activity(R_{eq}), representative level index (I_γ), external hazard (H_{ex}), internal hazard(H_{in}), Absorbed dose (AD), annual effective dose (AED) and excess life time cancer risk are 40.34 Bqkg^{-1} , 0.292, 0.108, 0.1316, 19.12 nGy.h^{-1} , 0.023 mSv.y^{-1} and $8.21 \times 10^{-5} \text{ Sv}^{-1}$.

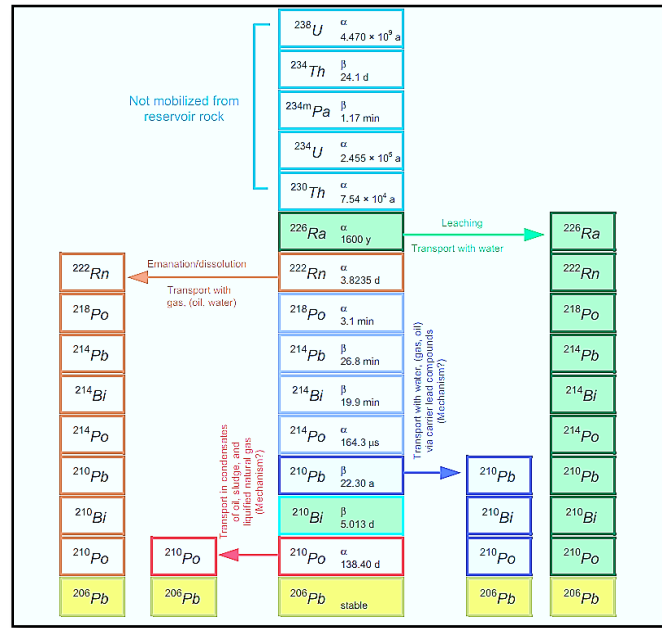
The hazard indexes (HI) from the LPG sample are less than one, indicating no health risk to human health for the above metals.

5.2. RECOMMENDATIONS

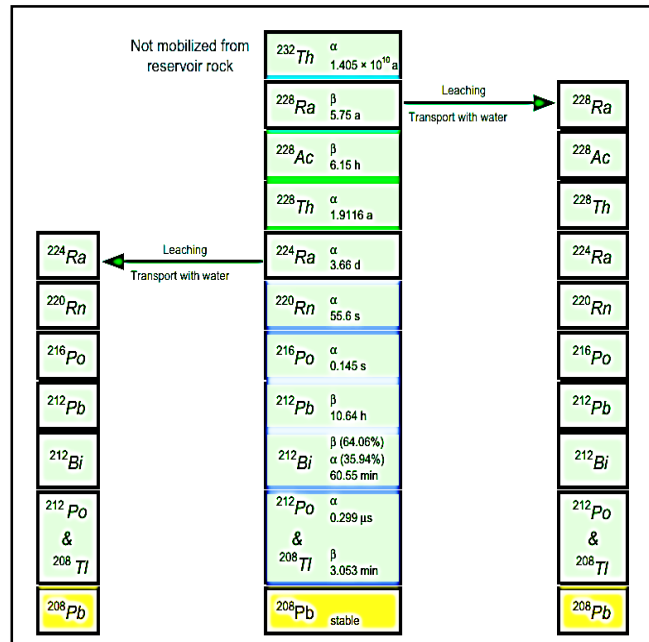
1. This article also suggests that the storage tank pressure and temperature can be considered as 10kg/cm² and 30°C filling the storage tank from the jetty to reduce LPG loss.
2. Instead of point/area modeling, a grid-based technique can be used to improve the modeling and analysis of radiation and the overpressure impact of releasing LP gas at various locations in the process area for future research.

APPENDICES

Appendix A1: Decay Series of ^{238}U for Radium Isotopes ^{226}Ra



(a)



(b)

Figure A.1: Decay Series of ^{238}U (a) for Radium Isotopes ^{226}Ra and (b) for ^{228}Ra and ^{224}Ra [54,55].

A.2 Heavy Metals in Soil of Different Country:

Table A.1: Heavy Metal in Soil of Different Country

Country	Heavy metals (mgkg ⁻¹)									Using device	Ref.
	As	Cd	Zn	Cu	Fe	Mn	Cr	Co	Pb		
Ethiopia	24.0-24.5	4.76-5.30	93.6-98.86	25.50-25.96	41410-46426	1696-1763	35.9-36.2	14.9-15.1	35.80-37.93	ICP-OES	[37]E
Bangladesh	37.5-42.3	0.84-2.02	97.7-444.7	36.83-87.66	34318-39864	595.-765	52.4-109.	8.01-16.8	<1.35-47.60	XRF	[13]E
Pakistan	22.3-23.1	4.21-4.54	91.3-94.56	21.32-24.36	51.32 - 56.28	1248-1341	23.2-25.6	7.31-7.56	32.12-33.4	AAS	[105]E
India	ND	0.45-23.8	24.7-62.83	4.65 - 33.95	ND	1.98-67.5	ND	3.34-13.5	4.16 - 21.60	AAS	[106]E
Greece	1.60-7.80	0.50-5.60	10.3-506	ND	20356-38830	ND	156 - 9923	12.1-23.2	ND	NAA, HPGe	[24]E
Italy	6.60 - 20.4	0.18-0.69	65.3-227	28.2 - 255.2	ND	ND	10.7 - 431	8.10 - 15.8	25.4 - 215	AAS	[34]E
China	21.4-92.9	1.39-7.51	148 - 605	24.60-372	2.69 - 9.07	405 - 7000	50 - 1240	6.20 - 14.2	68.50-236	ICP-MS	[2]E
Spain	12.8	0.19	89	27	32600	782	66	14.1	36	ICP-MS	[22]E
Bolivia	<0.1-179	<0.01-2.6	21 - 1295	1.9 - 77	ND	ND	ND	ND	8.2 - 295	ICP-MS	[109]E
Saudi Arabia	9.8 - 18.5	0.08-1.00	17.90-112	3.80 - 16.1	24000-48000	ND	3.2 - 41	1 - 4.5	3.2 - 41	ICP-MS	[126]E
Kenya	8.93	0.42	247.3	88.59	ND	ND	59.7	ND	26.87	ICP-MS	[127]E
Malaysia	0.28-280	0.01-2.02	2.9 - 137	0.37 - 114	ND	ND	0.10-72.7	0.05-38.7	0.55 - 90	ICPS, AAS	[128]E
Korea	2.85-704	0.001-12.8	89.7-1600	14.7 - 243	ND	ND	ND	ND	26.3 - 885	AAS	[129]E
Sri Lanka	0.56-3.56	ND	7.5 - 61.4	3.6 - 20.3	ND	ND	ND	ND	3.1 - 11.6	ICPS	[130]E
Nigeria	ND	0.15-3.84	1.51-89.84	ND	ND	11.1-95.93	0.00-53.8	ND	0.63 - 8.50	AAS	[131]E

*ND= Not detected

A.3 Concentration of Some Radionuclides in Different Country Soil

Table A.2 Some Radionuclides (^{226}Ra), (^{238}U), (^{228}Ra), (^{232}Th), and(^{40}K) in Different Country's Soil

Country	Radionuclides(Bqkg ⁻¹)			Measurement device	Reference
	^{226}Ra	^{232}Th	^{40}K		
Bangladesh	28.64-480.42	38.62-685.74	87.20-184.37	Gamma-spectrometer With HPGe detector	[13]E
Pakistan	24.72-78.48	21.73-75.48	298.5-570.8	Gamma-spectrometer With HPGe detector	[113]E
India	BDL-15.6	36.7-299.2	338.4-543.5	Gamma-spectrometer with NaI(Tl) detector	[136]E
Saudi Arabia	1.95-13.07	1.33-10.04	39.92-193.71	Gamma-spectrometer with NaI(Tl) detector	[137]E
Italy	24-231	20-70	242-1434	Gamma-spectrometer With HPGe detector	[112]E
Sri Lanka	7-41	32-84	516-876	Gamma-spectrometer With HPGe detector	[138]E
Turkey	46.05-68.83	9.29-50.57	325.89-530.02	Gamma-spectrometer with NaI(Tl) detector	[69]E
Nigeria	10.9-470.6	122.7-2189.5	BDL-166.4	Gamma-spectrometer with NaI(Tl) detector	[71]E
South Africa	10.52-64.86	4.52-45.11	62.70-604.80	Gamma-spectrometer With HPGe detector	[111]E
Vietnam	14.8-28.7	17.9-38.4	235-379	Gamma-spectrometer with HPGe detector	[117]E
Cyprus	0.01-39.3	0.01-39.8	0.04-565.8	Gamma-spectrometer with HPGe detector	[139]E
Palestine	8.8-127.8	4.4-44.8	34.3-404	Gamma-spectrometer	[140]E
Sri Lanka	7-41	32-84	516-876	Gamma-spectrometer with HPGe detector	[138]E
Slovenia	49-52	54-62	535-703	Gamma-spectrometer with HPGe detector	[141]E
Italy	24-231	20-70	242-1434	Gamma-spectrometer with HPGe detector	[112]E

*BDL= below detective level

*ND= not detected

A.4 Properties of Raw LPG Sample Collected from a Bottling Plant

Table A.3 Tested Properties of Raw LPG Collected from a Bottling Plant

Test Item	Unit	Method	Composite			
Collection Date			18.05.22	07.06.22	02.07.22	28.08.22
LPG Sample			Sample-1	Sample-2	Sample-3	Sample-4
Vapour Pressure @37.8°C	KPA	ASTM D2598	630.03	638.59	639.38	596.00
Total Sulphur	ppm	ASTM D6667	38.8	38.62	38.61	39.48
Free Water	-	Visual	NIL	NIL	NIL	NIL
Cu Corrosin, 1H@ @37.8°C	-	ASTM D1838	1A	1A	1A	1A
Density @15°C	Kg/L	ASTM D2598	0.5510	0.5502	0.5510	0.5505
Compositions:						
C2	wt%	ASTM D2163	0.08	0.08	0.08	0.08
C3	wt%	ASTM D2163	33.83	34.81	34.92	35.02
C4	wt%	ASTM D2163	65.96	64.98	64.70	64.77
C5	wt%	ASTM D2163	0.13	0.13	0.30	0.13
Butadiene	wt%	ASTM D2163	<0.01	<0.01	<0.01	<0.01
Residue on Evap @38°C	ml/100ml	ASTM D2158	<0.05	<0.05	<0.05	<0.05
Molecular Weight	-	Calculation	53.35	53.21	51.1	53.22
Odour	-	SMELL	Detectable	Detectable	Detectable	Detectable
Propane (C3 & Lighter Hydrocarbon)			33.91%	34.89%	35.00%	35.10%
Butane (C3 & Higher Hydrocarbon)			66.09%	65.11%	65.00%	64.90%

A.4 Tested Different Elements of the Soil, LPG and Crude Oil Samples

Table A.4 Total Elements of the Tested Soil and LPG Mixed Soil Samples

Element	Unit	LPS-1	±	LPS-2	±	LPS-3	±	LPS-4	±	LPS-5	±	LS-1	±
Na	[%]	0.789	0.024	0.844	0.026	0.726	0.023	0.768	0.024	0.749	0.023	0.674	0.021
Al	[%]	4.62	0.03	4.91	0.03	4.66	0.03	5.21	0.03	5.12	0.03	4.99	0.03
K	[%]	1.67	0.16	2.37	0.21	1.82	0.41	1.99	0.18	1.89	0.18	1.84	0.17
Sc	[µg/g]	15.57	0.10	8.69	0.07	13.19	0.09	11.39	0.08	14.35	0.09	15.11	0.10
Ti	[%]	0.37	0.03	0.43	0.03	0.46	0.03	0.37	0.03	0.36	0.03	0.37	0.02
V	[µg/g]	64	3	65	3	67	3	71	3	71	3	65	2
Cr	[µg/g]	152	4	93	3	164	4	126	3	170	4	164	4
Mn	[µg/g]	390	7	438	7	389	84	406	7	406	7	364	6
Fe	[%]	4.50	0.06	2.77	0.04	4.40	0.06	3.40	0.05	4.02	0.06	4.31	0.06
Co	[µg/g]	16.4	0.4	10.0	0.3	15.0	0.3	11.7	0.3	14.5	0.3	15.6	0.4
Zn	[µg/g]	73	4	61	3	23	2	53	3	75	4	87	4
As	[µg/g]	6.8	0.2	4.3	0.2	9.8	0.3	4.2	0.2	6.4	0.2	8.0	0.2
Br	[µg/g]	2.36	0.16	1.43	0.11	3.22	0.21	1.48	0.12	2.21	0.15	2.42	0.16
Rb	[µg/g]	228	14	132	9	252	15	161	11	215	14		
Sb	[µg/g]	0.77	0.03	0.41	0.02	0.86	0.04	0.46	0.03	0.58	0.03	1.78	0.05
Cs	[µg/g]	6.98	0.15	4.36	0.11	6.57	0.14	4.82	0.12	6.48	0.14	6.34	0.14
La	[µg/g]	55.42	0.86	37.45	0.67	69.31	1.08	37.65	0.69	59.55	0.91	69.55	1.00
Ce	[µg/g]	137	2	73	1	128	2	101	2	142	2	149	2
Sm	[µg/g]	9.884	0.041	6.348	0.031	13.144	0.052	6.166	0.031	9.979	0.041	10.626	0.043
Eu	[µg/g]	1.91	0.10	1.11	0.07	2.33	0.11	1.31	0.08	1.45	0.08	1.67	0.09
Yb	[µg/g]	5.13	0.25	2.75	0.17	8.38	0.36	4.09	0.23	5.23	0.26	5.30	0.26
Hf	[µg/g]	10.60	0.31	7.07	0.23	11.15	0.32	8.45	0.26	9.65	0.29	11.35	0.33
Ta	[µg/g]	1.83	0.16	1.24	0.12	2.08	0.18	1.14	0.12	1.56	0.14	1.48	0.14
Th	[µg/g]	29.73	0.45	15.54	0.29	26.79	0.42	20.20	0.35	28.53	0.44	35.76	0.51
U	[µg/g]	4.03	0.14	2.55	0.11	6.83	0.21	2.92	0.12	4.00	0.14	6.17	0.19

Table A.5: Elements Abundance in LPG Samples

Element	Unit	LPS-1	±	LPS-2	±	LPS-3	±	LPS-4	±	LPS-5	±
Na	[%]	0.134	0.004	0.143	0.004	0.123	0.004	0.131	0.004	0.127	0.004
Al	[%]	0.79	0.01	0.83	0.01	0.79	0.01	0.89	0.01	0.87	0.01
K	[%]	0.28	0.03	0.4	0.03	0.31	0.07	0.34	0.03	0.32	0.03
Sc	[µg/g]	2.65	0.02	1.48	0.01	2.24	0.02	1.94	0.01	2.44	0.02
Ti	[%]	0.06	0	0.07	0	0.08	0.01	0.06	0	0.06	0
V	[µg/g]	10.96	0.44	10.99	0.45	11.34	0.44	12.15	0.48	12.01	0.47
Cr	[µg/g]	25.91	0.6	15.87	0.43	27.8	0.63	21.43	0.54	28.84	0.65
Mn	[µg/g]	66.32	1.13	74.51	1.25	66.12	14.31	69.01	1.19	68.96	1.18
Fe	[%]	0.76	0.01	0.47	0.01	0.75	0.01	0.58	0.01	0.68	0.01
Co	[µg/g]	2.79	0.06	1.7	0.05	2.56	0.06	1.99	0.05	2.46	0.06
Zn	[µg/g]	12.36	0.6	10.44	0.53	3.92	0.31	9.03	0.5	12.68	0.61
As	[µg/g]	1.15	0.04	0.72	0.03	1.66	0.05	0.71	0.03	1.09	0.04
Br	[µg/g]	0.4	0.03	0.24	0.02	0.55	0.04	0.25	0.02	0.38	0.03
Rb	[µg/g]	38.8	2.36	22.45	1.6	42.85	2.55	27.43	1.9	36.5	2.3
Sb	[µg/g]	0.13	0.01	0.07	0	0.15	0.01	0.08	0	0.1	0
Cs	[µg/g]	1.19	0.03	0.74	0.02	1.12	0.02	0.82	0.02	1.1	0.02
La	[µg/g]	9.42	0.15	6.37	0.11	11.78	0.18	6.4	0.12	10.12	0.16
Ce	[µg/g]	23.37	0.33	12.49	0.22	21.7	0.31	17.21	0.28	24.2	0.34
Sm	[µg/g]	1.68	0.01	1.08	0.01	2.23	0.01	1.05	0.01	1.7	0.01
Eu	[µg/g]	0.32	0.02	0.19	0.01	0.4	0.02	0.22	0.01	0.25	0.01
Yb	[µg/g]	0.87	0.04	0.47	0.03	1.42	0.06	0.7	0.04	0.89	0.04
Hf	[µg/g]	1.8	0.05	1.2	0.04	1.9	0.05	1.44	0.05	1.64	0.05
Ta	[µg/g]	0.31	0.03	0.21	0.02	0.35	0.03	0.19	0.02	0.27	0.02
Th	[µg/g]	5.05	0.08	2.64	0.05	4.55	0.07	3.43	0.06	4.85	0.07
U	[µg/g]	0.68	0.02	0.43	0.02	1.16	0.04	0.5	0.02	0.68	0.02

A.5: Program of Weight Calculation

```
#include<stdio.h>
#include<math.h>
#define P 1.01325 //atmospheric pressure kg/cm2
#define R 247.7 //R, expand ratio=liquid/vapor
#define pa .0011 //density of the air
main()
{
    float w,vn,pl,vl,vv,v,v1,v2,v3,P1,P2,P3,T1,T2,t1,t2,CF;
    printf("enter the capacity of the tank:");
    scanf("%f",&v);//capacity of the sphere
    printf("enter the vapor pressure at given temperature:");
    scanf("%f",&P3);//P3 is the given vapor pressure
    printf("enter the density of the LPG:");
    scanf("%f",&pl);//pl is the density of liquid
    printf("enter the given temperature:\n");
    scanf("%f%f",&T1,&T2);//celcius temp+273
    printf("volume of the LPG_mix:\n");
    scanf("%f",&v3);
    printf("enter the correction factor of the volumn at observed temp:\n");
    scanf("%f",&CF);//using ASTM 54 table
    P1=P3+P;//observed pressure
    P2=P;
    v1=v-v3;//vapor volume
    vl=v3*CF;//liquid volume
    t1=T1+273;
    t2=T2+273;
    v2=(P1*v1*t2)/(t1*P2);
    //total volume at NTP
    vv=v2/R;//vapor volume at NTP
    vn=(vl+vv)*1000;//total volume at NTP(liter)
    w=(vn*(pl-pa))/1000;
    printf("the weight of the LPG(MT)=%f",w);
    return 0;
}
```


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