

Continuous Measurement of Odorant Composition for Liquefied Petroleum Gas

Rodrigo J. Seguel*, Carlos A. Mancilla, Pablo A. Sakamoto

Environmental Department, Trade & International Advisory SAGU, Los Canteros 8666, Parque Industrial de La Reina, Santiago 7880340, Chile
roseguel@icloud.com

In Chile, commercial liquefied petroleum gas (LPG) is customarily odorized with dimethyl sulfide (DMS) and tert-butyl mercaptan (TBM) at a rate of about 10 grams of odorant per 1 cubic meter of LPG. The current control of the odorization practice involves the human nose to detect the odor in some cases, and the determination of total sulfur concentration in others. None of those methods provide the speciation of the sulfur species in LPG.

On the other hand, both DMS and TBM are higher boiling than propane or butane. Therefore, the odorant concentration emanating from the odorized liquid is not uniform in the vapors released. Furthermore, the gas will also be much leaner than the odorized liquid. For those reasons, the Chilean industry recommends analyzing the odorant directly from the liquid phase.

To address the problem of odorant quantification at the industry this research aims to develop a reliable and objective measure for odorized LPG that allow not only verify the odorization itself but also quantify the species incorporated with the fuel, and other sulfur compounds present naturally in the LPG. In this regard, an Automated Gas Chromatograph (Auto-GC) with an electrochemical detector was coupled with an LPG valve, which continuously takes samples of 1 μL of liquid propane. The extracted sample is then vaporized and injected into the Auto-GC to be analyzed.

The methodology is capable of distinguishing and quantifying distinct odorants near real-time (within 8 minutes), as well as other sulfur impurities present in the LPG such as tetrahydrothiophene (THT) and methyl mercaptan (MeSH). Typical retention times for TBM and DMS corresponded to 282 s and 418 s respectively. More importantly, the proposed method provides meaningful information to verify the optimum odorization, i.e., the minimum value to alert in case of leak and maximum level that assures efficient combustion.

1. Introduction

LPG is the term applied to certain light hydrocarbons and their mixtures, which exist in gaseous state under atmospheric ambient conditions. LPG can be easily converted to the liquid state under conditions of moderate pressure at ambient temperature. The principal constituent of LPG is propane. Other constituents are ethane and butanes. Because propane, the major component of LPG, has a faint petroleum-like odor (NCBI, 2018), the addition of odorants is required by regulation to assure the presence of the gas can be detected readily in case of accidents and leaks.

The odorization is provided by the addition of trace amounts of organic sulfur compounds such as DMS and TBM to the LPG before it reaches the consumers. The national standard requirement established that a user will be able to detect the presence of the LPG by odor when the concentration reaches 0.48 % of gas in air, equivalent to one-fifth the lower limit of flammability of propane (~2.4%) (INN, 1999).

Currently, in Chile, the effectiveness of the odorization process is determined by a subjective method that uses the human nose to detect the odor; the so-called sniff test. Despite its apparent simplicity, the implementation among gas companies has not been entirely satisfactory because this method involves the judgment of employees to detect the presence of odor. Difficulties such as the decrease in the panelist olfactory capacity exposed to consecutive measurements of gas, or variations due to the different olfactory

sensitivity among employees, are common issues in this kind of practice (Stevens et al., 1987). For these reasons, the international regulation has been moving toward objective measurements (ASTM, 2008).

Arguments to establish alternative methods include:

- (a) Some individuals possibly experience a chronic or transient decrease in the olfactory system and as a consequence cannot detect the odorants properly.
- (b) In work environment, the odorants often appear masked with other odors that impede to discriminate them.
- (c) Extended exposure periods may cause olfactory fatigue in workers exposed to odorized fuels making difficult to recognize the presence of odor and their variations.
- (d) Chemical reactions consuming odorants may occur. This loss may affect new pipes, whose inner walls contain oxides capable of reacting with the odorant. This phenomenon can also occur in existing pipes of large diameter and length.

By contrast, instrumental analysis methods based on physicochemical principles provide information about the identification and quantification of the chemical species associated with odors (Vera et al., 2016). This chemical approach allows monitoring impurities naturally present in commercial propane. For example, carbonyl sulfide (COS) as other sulfur species can hydrolyse to form hydrogen sulfide (H₂S), a corrosive species (Andersen et al., 2003).

Furthermore, achieving the optimum range of odorants in the fuel is beneficial beyond the primary goal of alerting in case of leakage, because it prevents the excess of sulfur compounds from reducing efficient combustion and therefore generating an economic loss for consumers. For these reasons, this research aims to provide the national natural gas and petroleum industry with a reliable alternative solution for the on-site objective control of mercaptans in gas pipelines, in truck terminals, and storage tanks. The method comprises a gas chromatograph coupled with an electrochemical detector integrated to an automatic LPG valve.

The implementation of this methodology would allow the industry to: (1) Optimize the odorization process by reducing the excess of added mercaptans. (2) Increase the speed of gas distribution from truck terminals through a quick and reliable analysis. (3) Minimize the time consumption in storage plants due to operational activities that correct the non-compliance of odorization levels regulated by the authority. (4) Reduce the corrosion of gas pipelines caused by sulfur species. (5) Quantitatively verify the regulatory compliance of odorization in gas shipped by trucks.

2. Methodology

2.1 Instruments and apparatus

The quantification of DMS and TBM from the liquid phase of the LPG was performed using a Chromatotec model EnergyMedor automated gas chromatograph (autoGC) coupled to a specific electrochemical detector containing chromic acid solution at 10%. The auto GC is equipped with 2 metallic columns of 4 m and 30 m (0.53 OD), which improve the separation process.

The sampling of LPG from the cylinder was accomplished using a valve specifically designed to extract representative samples from the liquid phase. During the analysis, a total volume of 1 µL of LPG is expanded and then transferred to the autoGC to determine the composition.

A second Chromatotec model TRS Medor autoGC was used to compare results from liquid phase with the gas phase.

2.2 Sulfur compounds method

A routine method was created to analyze 14 sulfur compounds in a 30 min cycle. Nitrogen was used as a carrier gas at a pressure of 195 hPa (\pm 1 hPa) at the column head, and the temperature of the column was kept isothermally at 58 °C.

2.3 Odorization

At the marine terminal, the LPG is odorized through an YZ odorization system, which injects precise amounts of commercial liquid odorants (70 % of DMS and 30 % of TBM) into the LPG pipeline. Both substances have low odor threshold mixing ratios (OTMR) and characteristic odor, which as mentioned above, allows alerting gas leaks. Table 1 shows the odorants incorporated and their physical and chemical properties. It is worth noticing that the boiling point of the odorants and propane are substantially different. The same marked differences can be observed in the vapor pressure.

Table 1: Physical and chemical properties of dimethyl sulfide, tert-butyl mercaptan and propane (Lide, 2007; Daubert and Danner, 1989; Nagata and Takeuchi, 1990).

Compound	CAS number	Structure	Molecular weight (g/mol)	Boiling point (°C)	Vapor pressure (mmHg @ 25 °C)	OTMR (ppbv)
Dimethyl sulfide	75-18-3	(CH ₃) ₂ S	62.13	37.3	502	3
Tert-butyl mercaptan	75-66-1	(CH ₃) ₃ CSH	90.184	63.7 - 64.2	181	0.029
Propane	74-98-6	CH ₃ CH ₂ CH ₃	44.097	-42.1	7,150	-----

2.4 Samples

Odorized HD-5 propane samples were collected in steel cylinders from the marine terminal on September 12, 2017, November 23, 2017, and January 23, 2018. After sampling, the cylinders filled with 3.8 L of propane were sent to the laboratory within 24 hours to be analyzed. However, the holding time never exceeded 14 days from the sampling until the analysis to avoid any degradation of sulfur compounds over time (Haerens et al., 2016).

2.5 Reference material

A certified reference material was used to quantify DMS and TBM. Table 2 shows the concentration certified in propane matrix.

Table 2: Primary standard composition.

Compound	Concentration (mg/kg)	Concentration (mg/L)	Accuracy
Dimethyl sulfide	28.9	17.2	± 1%
Tert-butyl mercaptan	10.0	6.1	± 1%
Propane	99.996	99.998	± 1%

2.6 Odor activity

The ratio of the mixing ratio of a compound to its odor threshold (MR/OTMR), also known Odor Activity Value (OAV) was used to determine the strength of the odorants (Cariou et al., 2016; Patton and Josephson, 1957). These relative ratios, rather than absolute MR, provide a useful measure of the odor intensity in a mixture.

3. Results and discussion

3.1 DMS and TBM quantification

A chromatographic run of 8 min allows separating both analytes of interest from the LPG sample. Figure 1 shows the typical chromatogram associated with the primary standard.

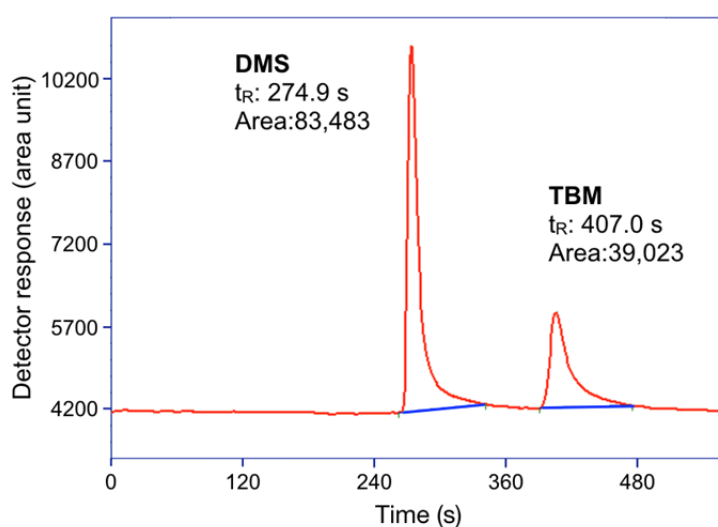


Figure 1: Chromatogram obtained through a gas chromatograph coupled with an electrochemical detector integrated to an automatic LPG valve.

Table 3 shows the retention time (t_R) associated with DMS and TBM. The average DMS concentration corresponded to 17.4 mg/kg, and the coefficient of variation (CV) was 4.3 %. For TBM, the average concentration and CV corresponded to 6.25 and 3.4 % respectively. The DMS to TBM ratio was slightly different compared with the theoretical ratio (70:30) probably due to the higher reactivity of TBM.

Table 3: Retention time and concentration of odorants (DMS and TBM) in LPG sampled on January 23, 2018.

t_R of DMS (s)	t_R of TBM (s)	DMS (mg/kg)	TBM (mg/kg)	Ratio DMS: TBM	Odorants (mg S/kg)	Odorants – Total S (mg S/kg)
278.5	412.9	17.7	6.4	73.4 : 26.6	11.4	-3,3
281.1	416.1	18.3	6.2	74.6 : 25.4	11.7	-3,0
282.1	417.7	17.3	6.3	73.2 : 26.8	11.2	-3,5
283.9	420.1	17.6	6.4	73.3 : 26.7	11.3	-3,4
285.5	423.2	16.3	5.9	73.4 : 26.6	10.5	-4,2

3.2 Other sulfur compounds identification

The difference between the total sulfur (14.7 mg S/kg) and the sum of DMS and TBM is shown in Table 3. This difference (3.5 mg S/kg) can be explained by the presence of two sulfur species others different than added during the odorization process (Figure 2). The identification of those species was accomplished using the retention time previously set on the TRS Medor based on a mixture of external standard gas. The species were THT (~40 s) and MeSH (~182 s).

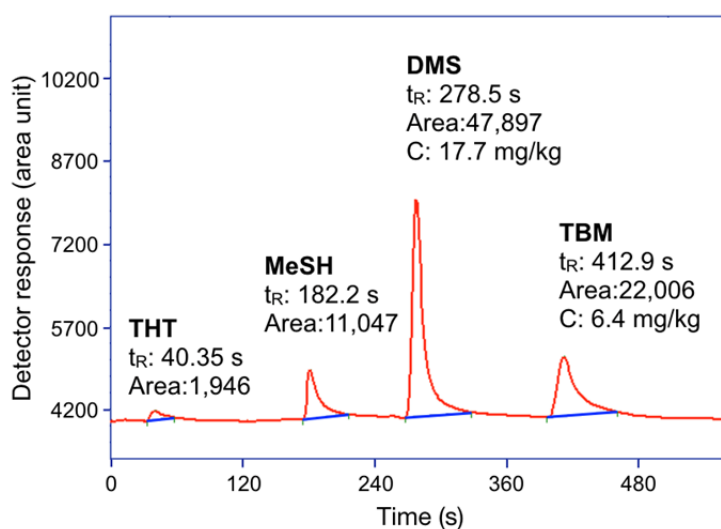


Figure 2: Chromatogram obtained with an electrochemical detector and using an LPG valve. Typical chromatogram of odorized LPG samples detected 4 species within 10 minutes.

3.3 DMS and TBM mixing ratio

The mixing ratios equivalent to one-fifth the lower limit of flammability of propane was calculated from the average concentration measured in LPG. A density of 0.5063 kg/L at 15 °C and an expansion factor of 272.6 were used. Estimated mixing ratios of 61 and 15 ppbv were obtained for DMS and TBM respectively. These mixing ratios exceed the OTMR (Table 1) and thus assured the objective of odorizing. Also, the measured mixing ratios of DMS (12.7 ppmv) and TBM (3.1 ppmv) were well above the instrument limit of quantification corresponding to 0.058 and 0.036 ppmv respectively. This exercise is an example where the combination of instrumentation and sense of smell can assist for appropriate control of the odorization practice.

On the other hand, the lower relative content of TBM in LPG and the higher reactivity toward OH radical are compensated by the higher OTMR (Table 4).

Table 4: Odorant concentration (C) in LPG and calculated odorant mixing ratio in air equivalent to one-fifth the lower limit of flammability of propane.

Compound	C in LPG (mg/kg)	C ($\mu\text{g}/\text{m}^3$)	Mixing ratio (ppbv)	Odor activity value (OAV)
DMS	17.4	155	61.1	20.4
TBM	6.25	55.7	15.1	521

3.4 Benefits of controlling the odorization process

The accurate application of odorants is critical in the fuel gas industry not only for attaining the required warning but also due to the effects that the excess of odorants may produce in the combustion. Commonly excessive odorants affect the combustion of the gas and produce sooting.

Accordingly, Figure 3 shows the points where it is recommendable to verify the level of odorants in odorized LPG shipped via either pipelines or trucks throughout the entire transportation cycle.

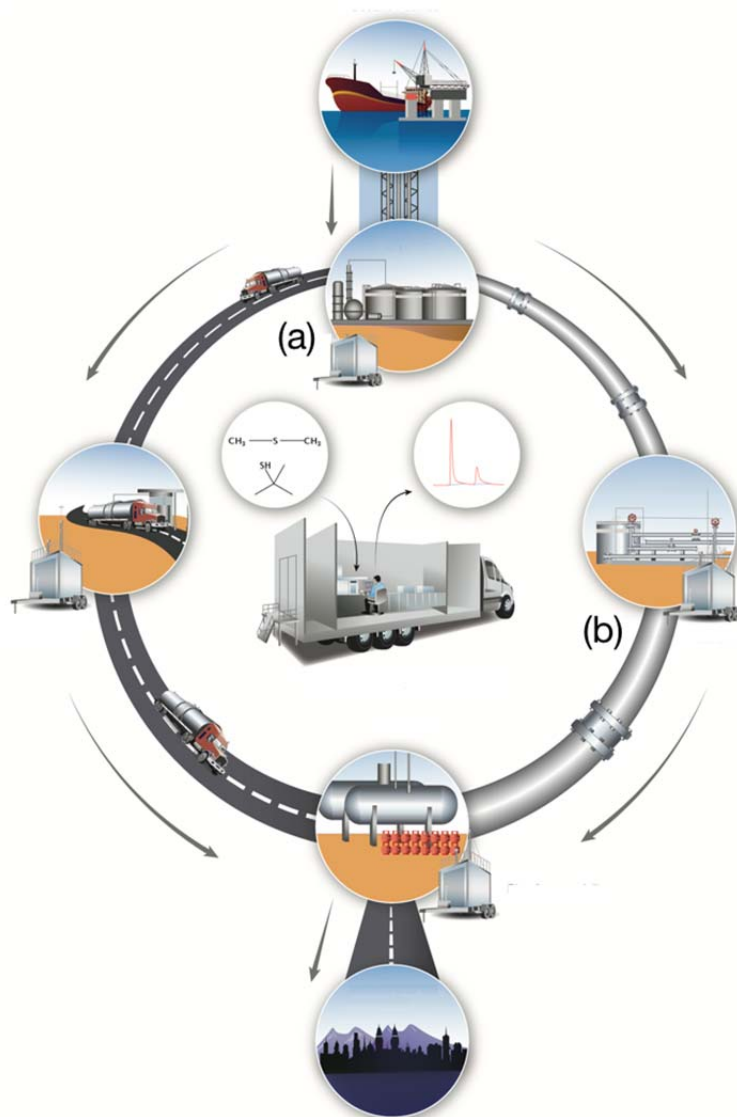


Figure 3: Representative points throughout the distribution system where it is recommended analysing the odorant blends. The scheme singles out the odorization points: (a) marine terminal before truck distribution and (b) end of the pipelines before distribution to consumers.

4. Conclusions

Automated Gas Chromatograph coupled with an electrochemical detector is an accurate method to separate several sulfur compounds for identification and quantification. The system operates continuously, on-site, and remotely. However, the instrumentation requires trained personnel to supervise the analysis.

An automatic valve able to extract precise quantities of liquefied petroleum gas from the liquid phase is necessary to achieve quantitative results. Dealing with liquid phase improves the reproducibility by avoiding the differences of boiling points between odorant blends and propane.

The average concentration of dimethyl sulfide and tert-butyl mercaptan found in liquefied petroleum gas corresponded to 17 and 6 mg/kg respectively. Those levels comply the national standard requirement.

The mixing ratio in the air, equivalent to one-fifth of the lower flammability limit for dimethyl sulfide and tert-butyl mercaptan was 61 and 15 ppbv respectively. Both values are higher than the odor thresholds and therefore readily detectable by the olfactory system of an average person.

Acknowledgments

The authors acknowledge the financial support from CORFO, InnovaChile program, Project N° 16IDAE-67661.

References

- ASTM (American Society for Testing and Materials), 2008, Standard Test Method for Online Measurement of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatograph and Electrochemical Detection (D7493-08), ASTM International, West Conshohocken, PA.
- Andersen, W.C., Abdulagatov, A.I., Bruno, T.J., 2003, The ASTM copper strip corrosion test: application to propane with carbonyl sulfide and hydrogen sulfide, *Energy & Fuels* 17, 120-126.
- Cariou S., Chaignaud M., Montreer P., Fages M., Fanlo J.L., 2016, Odour concentration prediction by gas chromatography and mass spectrometry (gc-ms): importance of vocs quantification and odour threshold accuracy, *Chemical Engineering Transactions*, 54, 67-72 DOI: 10.3303/CET1654012
- Daubert, T.E., R.P. Danner, 1989, *Physical and Thermodynamic Properties of Pure Chemicals Data Compilation*, Washington, D.C., Taylor and Francis.
- Haerens K., Segers P., Van Elst T., 2016, Sampling and stability of mercaptans: comparison between bags, canisters and sorbent tubes, *Chemical Engineering Transactions*, 54, 31-36 DOI: 10.3303/CET1654006
- Lide, D.R., 2007, *CRC Handbook of Chemistry and Physics 88th Edition 2007-2008*. CRC Press, Taylor & Francis, Boca Raton, FL, p. 3-210
- Nagata, Y., N. Takeuchi, N., 1990, Measurement of odor threshold by triangle odor bag method, *Bull. Jpn. Environ. Sanit. Cent.*, 17, 77-89.
- NCBI (National Center for Biotechnology Information), 2018, PubChem Compound Database <<https://pubchem.ncbi.nlm.nih.gov/compound/6334>> accessed 10.04.2018.
- INN (National Institute for Standardization), 1999, Chilean standard (NCh2394.Of1999), Liquefied petroleum gases and natural gas – odour test.
- Patton, S., Josephson, D.V., 1957, a method for determining significance of volatile flavor compounds in foods, *Journal of Food Science*, 22(3), 316-318, doi:10.1111/j.1365-2621.1957.tb17017.x.
- Stevens, J.C., Cain, W.S., Weinstein, D.E., Pierce, J.B., 1987, Aging impairs the ability to detect gas odor. *Fire Technology* 23, 198-204.
- Vera L., Companioni E., Meacham A., Gigax H., 2016, Real time monitoring of VOC and odours based on gc-ims at wastewater treatment plants, *Chemical Engineering Transactions*, 54, 79-84 DOI: 10.3303/CET1654014