2022

Comparison of Fresh and Used Refrigerator Compressor Oil Properties with GC-MS, GC-SIMDIS and ICP-MS Analysis

Gizem Balkız

Husnu Kerpicci

Nuray Gulmez

Emre Oruc

Aysegul Mericboyu

Comparison of Fresh and Used Refrigerator Compressor Oil Properties with GC-MS, GC-SIMDIS and ICP-MS Analysis

Gizem Balkız[1]*, Hüsnü Kerpiççi[2], Nuray Gülmez[2], Emre Oruç[3] Ayşegül Meriçboyu[3]

[1]Istanbul Technical University, Chemical Engineering Department,
Istanbul, Turkey
Gizem Balkız (+905325273963, gizem.balkiz@arcelik.com)

[2]Arçelik A.Ş., Central R&D Department,
İstanbul, Turkey

[3]Arçelik A.Ş., Eskisehir Compressor Plant R&D Department,
Eskisehir, Turkey

* Corresponding Author

ABSTRACT

Nowadays, sales of new refrigerators amount to 150 million units annually. Also, electricity consumption resulting from the use of refrigerators and cooling devices constitutes %6 of the global electricity consumption. Energy regulation and labelling which came in force last year urge all manufacturers to pull up the energy efficiency of all products. Since compressor is playing a heart-like role in the refrigerator energy efficiency, most of the engineering studies lens on the improving performance of the refrigerator compressors.

Basically, dividing performance of the compressor in three main parts such as electrical motor, thermodynamic and mechanical, compressor oil can be classified as main issue affecting not only mechanical efficiency but also reliability of the compressor. Therefore, research on understanding petrochemical ingredients in lubricating oils become an evolving field in recent years. From this point of view, ensuring higher mechanical efficiency in compressors basically depends on the improvements in the lubricant.

In this study, three different compressor oils have been chosen which have different chemical contents and viscosities. The performance of the oils has been evaluated with enhanced lifetime tests which simulate harsh operating conditions in the field. Used oils have been analyzed after the lifetime tests. The results between fresh oil and used oil have been compared. GC-MS and GC-SIMDIS have been used to determine organic molecules and their structural changes. Moreover, ICP-MS has been used for the inorganic particle changes. The main purpose of this study is to determine the compressor oil contents and how these structural changes could cause an effect over the wearing properties of the compressors. With developing these analysis and make the comparison between the oil and their used version, it can be simulated which oil is more effective for the compressor system than the others.

Index Terms – Lubrication Oil, Refrigerator Compressor, GC-MS, GC-SIMDIS, ICP-MS

1. INTRODUCTION

Lubricants are critical to machinery element safety. Their primary tasks include: Putting away to the compressor parts from each other, help to cool down the contact through the aisle, making the surface clean, carrying the functional additives to the regarding areas. (Holweger, 2013). Lubricants are widely used in the worldwide. Until the data of 2007, it has seen that sales of the lubrication related to the 37% of hydraulic oil, 7% of the industrial gear oils, 16% of the metalworking fluids and 9% of greases. (Mang, 2007).
Lubricants are classified as hydrocarbons, ester oils, and polyglycoles. In general term, based on the hydrocarbon and double bond contents, sulfur content and the viscosity index range determines the group of oils. These classifications

begin Group I and follows with the Group II, III, IV, V. In terms of the usage area and the consumer needs, one of the following Groups of oils can be chosen. Their chemical contents would give a clue about the performance characteristic of the compressor.

Lubrication oil working mechanism is also related with the temperature and the pressure. Under high temperature and the pressure conditions, oil viscosities reduce and the protection layer thickness become thinner. At this circumstances, thin layer causes defection the metallic parts. (Yücel, 2005)

The present paper aims to find an experimental approach between different type of oils which have also different viscosities, with the effect of temperature and pressure. Determination of the mineral oil [MO] contents with the GC-MS is well-known technique regarding organic analysis. Organic structures with the LC, GCxGC analysis have been monitored in the recent analysis. (Bauwens, 2021) Considering classification of the analysis GC-FID was observed to be less separation efficiency compared to the HPLC-GC combination analysis. (Yan-Wen, 2021) Regarding GC analysis, for the MO, the most important factor that has to be considered is the method development on the analysis parameters. GC parameters determination is worked with the recent studies and optimized for the MO. (Greye, 2016)

The experimental part separated from each other as organic and inorganic analysis. Over the organic analysis molecular weight calculation and the carbon chain distribution were the main stone of the analysis. In the inorganic part, elements that have been found at the fresh oil were basic reference point of this analysis. Changes over the fresh oil with the result of the temperature and the pressure can also be detected. Inorganic elements can be found on the inner surface of the compressor and surface of the working metallic parts. So, the materials which have been used for manufacturing of these parts, hold a serious importance as well.

In this paper, new compressor test system has been developed. 3 different temperature and pressure conditions have been selected. 3 determined test conditions have applied individually each different compressor which have different types of oils. While used and unused oil contents analysis have been performing, the wear properties of the used compressors have also determined. With the analysis results and the wearing characteristics put together to understand the mechanism.

2. EXPERIMENTAL AND TEST PROCEDURE

2.1. Organic Analysis

Gas chromatography is an effective separation technique. In this technique, there is a stationary phase which holds the unrequired materials in its composition and there is a mobile phase which goes through the column to separate and transfer the required analytes from the sample to the detector. (Greye, 2016)

In this paper, MS (mass spectroscopy) and the FID (Fourier ionization detector) have been used for the analysis. MS is a detector to detect the molecular formulation based on the molecular weight of the analytes. As seen in the equation (1), with this technique 70eV electron beam energy is obtained with removal a single electron from the molecule. (Greye, 2016)

$$M = M^{+\bullet} + e^{-} \qquad (1)$$

FID detector on the other hand has used for SIMDIS (simulated distillation) analysis for the determination of the carbon chain distribution on the lubrication oil samples. With these both organic analysis methods, all the necessary.

GC analysis has performed with QP2020 Shimadzu. As a solvent solution, n-heksane (97%, Sigma Aldrich) was used. Column is DB5MS and the samples were feeded to the system with the diluted ratio 1:100. The injection volume was 1 µ/L, column temperature was heated up the 380 ºC through 60 minutes analysis time. He is used as a carrier gas for the system. The test method developed from the experimental studies of He *et al.*. (He, 2015).

In the FID Analysis DB-HT SIMDIS column was selected. A carrier gas was He. As a solvent CS_2 (carbon disulfide) was used as a reagent to the SIMDIS analysis. The injection volume was 1 µ/L as same as GC-MS. Also the column

temperature was raised up to 350 ºC step by step with the each 25 minutes period. For this SIMDIS analysis, the inspiration of the experimental work belongs to Fujinary *et al* is absorbed. (Fujinary, 1998)

2.2. Inorganic Analysis

In terms of the analytical sensitivity, inductively coupled plasma mass spectroscopy (ICP-MS) has long been known to be a well-established method for analyzing multi-element compounds, particularly at traces and ultra traces. Especially, when considering quantification analysis, ICP-MS is more simply method regarding liquid standard determinations. In ICP-MS technique, the matrix effect compared to the other techniques, has very high sensitivity suc as the ppb (parts per billion). (Telgmann, 2016). Ar (Argone) temperature gets higher up to the 600-700 ˚C. Then the Ar carries the samples as plasma and make them ionized. After separation the elements regarding the mass/ load, samples detected from the detector.

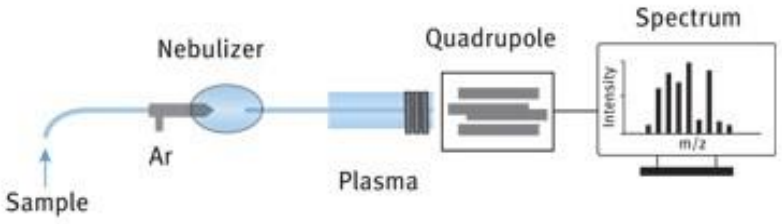


Figure 1 : Systematic diagram for ICP by Telgmann (2016)

Sample preparation is one of the most important factor in the ICP-MS analysis. To be able to trace the inorganic metal ingredients, first, the organic content of the sample has to be burned and removed from the environment. Then the crude part of the sample could analyzed. Muller *et al*, used similar analyzing methods in their experiments for creating the ICP-MS method. (Muller, 2016)

In this study, Milestone Ethos Easy 2016 Model Microwave Owen has selected for removal of the organic part of the lubrication oil. Each oil sample weighted as 0.1g then respectively 8 ml of H_2O_2 and 5 ml of HNO_3 were added over the samples. After the shaking process, vessels were put to the microwave system and with the two steps of the ramp processes has applied. At this point of view, the samples were ready to the ICP-MS analysis.

Calibration solutions were prepared from %3 diluted HNO_3 solution beginning with the 5 ppb to 50 ppb for ICP-MS analysis. When the calibration processes has finished, the prepared crude oil samples had feed to the ICP-MS.

2.3. Viscosity

In this experiment kinematic viscosities have been measured for the comparison between the lubrication oil samples. (Wilke) Schoott-Gerate model is used in the Ubbelohde viscometer for the determination of the viscosity.

3. RESULTS AND DISCUSSION

3 different refrigerator compressor oils have been analysed with GC-MS, GC-SIMDIS and ICP-MS.

All analysis has helped to understand the original versions of the oils. Results of the inorganic and organic structure of these 3 oils were determined. Deficiencies over the compressor oil has observed with the test system which is under different temperature and pressure effects.

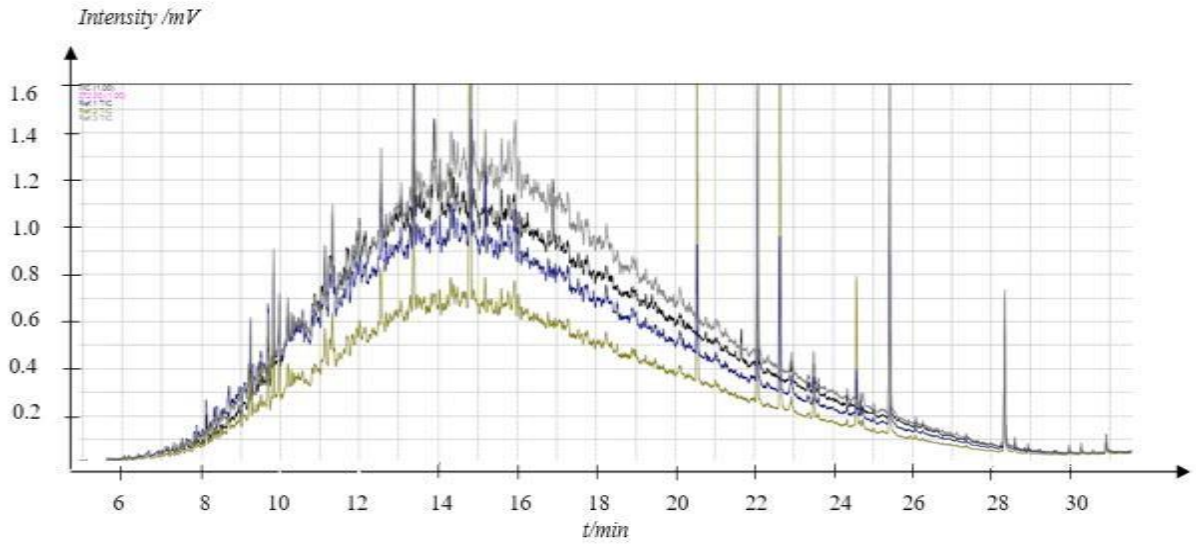
In the compressor systems, 3 different test conditions have determined for 72 hours long. 90 ˚C and 150 ˚C were selected as temperature gradients, 15 bar and 30 bar were selected as pressure gradients. Combination of these conditions have applied for the oils in the test setup then the used oils have been taken from the compressors and analysed with GC-MS, GC-SIMDIS and ICP-MS just like the same condition of their original version.

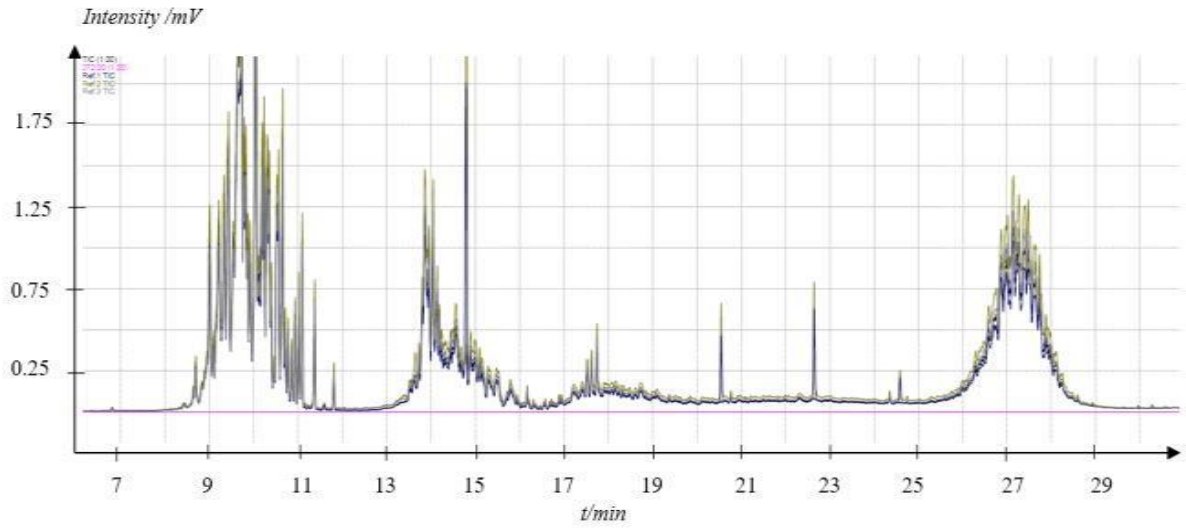
In this way, original oils with the viscosity of the 9 cSt, 7 cSt and 5 cSt and their used version which are faced with 3 different test conditions were compared with each other.

3.1.GC-MS Results

Original version of the 3 different oil content is figured out from the GC-MS chromatograms. Based on the analysis results, it showed that 9 cSt oil has more paraffinic structures. Beside to the paraffinic content, aromatic rings and some naphthenic groups have been detected into the oil. Every mineral oil has these base oil structures in their composition but only differences of the considering the percentage of these groups. Krasodomski et al, also used GCMS technic for to monetarise the n-paraffin, isoparaffin, naphthelenes and other groups in the oils. (Krasodomski, 2010)

GCxMS chromatogram has showed that 7 cSt oil is a mixture of 3 different base oil. And based on its contents it is more likely paraffinic and naphthenic. Last oil analysis also showed that 5 cSt oil has more aromatic and naphtenic contents in its composition. Paraffinic chemical structures were also found in the formulation less than the other groups.





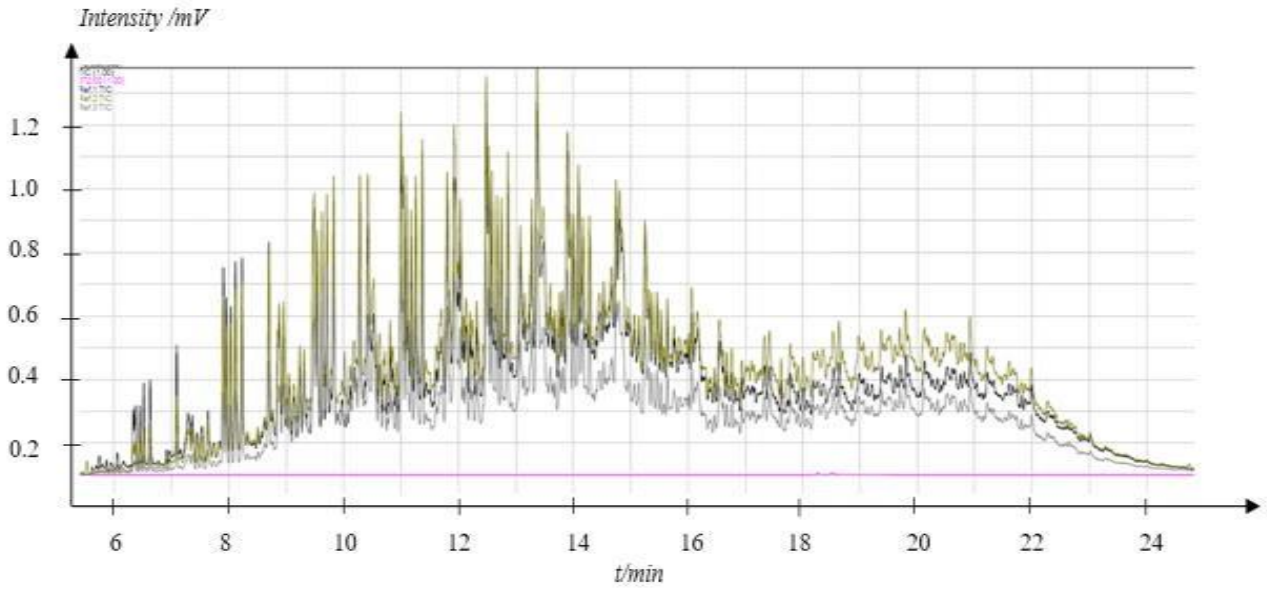


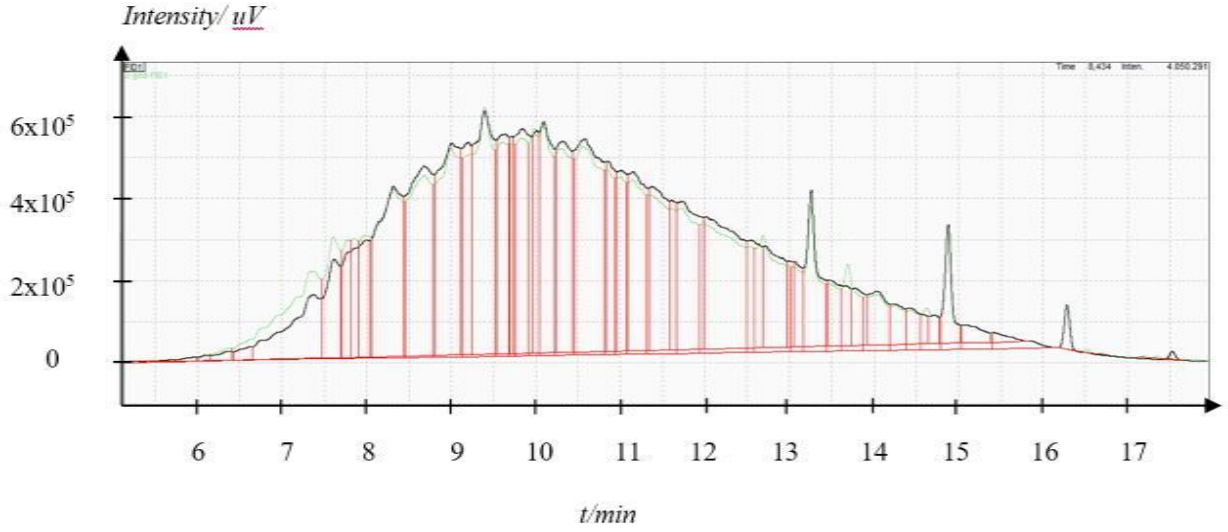
Figure 2 : GC-MS Results for 9 cSt, 7 cSt and 5 cSt oil with their used version

In the Figure 2, used oils and original oils were also seen with the together in the same graph and then some new chemical structures has been found on the analysis. These structures formation can be considered as oxidation results. Additionally, some of the anti-wear additives and extreme pressure additives breaking were also changed in the structure of these chemical groups and their new formulation were found in the composition. Same results were detected on the second graph for the compressor oil with the 5 cSt as well. The breaking of the chemical groups and the oxidation groups have been detected. On the other hand, the composition is protected as its original version for 7 cSt oil. It can be easily said that the stronger chemical would not change under temperature and the pressure effects.

3.2.GC-SIMDIS Results

Mineral oils carbon chain distribution and their molecular changing regarding temperature and the pressure have also been detected in the GC-SIMDIS analysis. The original form of the 3 refrigerator compressor oil and their used version were analysed.

In the Figure 3, for both 9 cSt oil, 7 cSt oil and 5 cSt oil, the breaking of the carbon chains was seen in the same regions. Decreasing over the chain between C14 to C18 monitored as decreasing while from C17 to C20 regions shows increasing path.



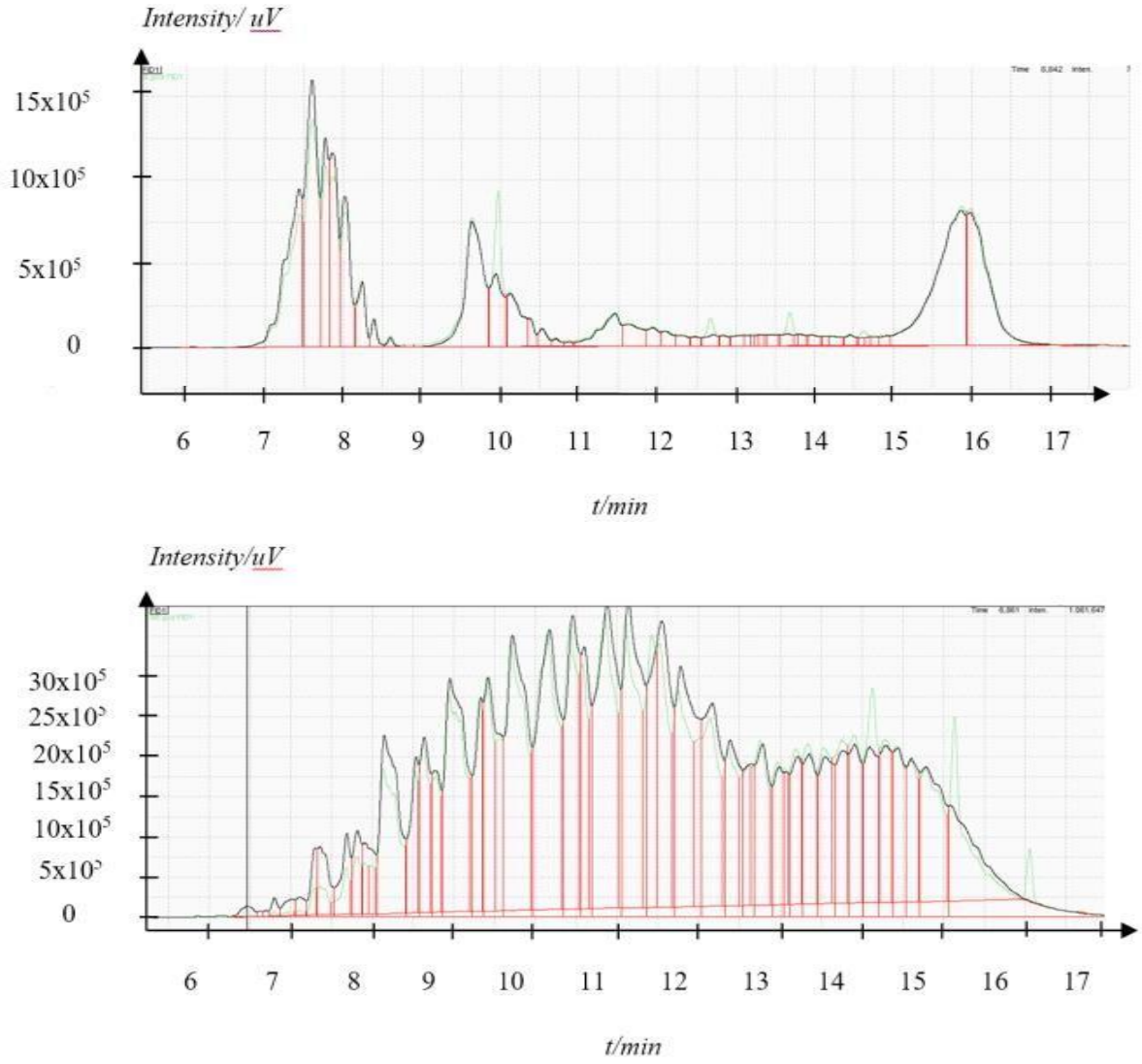


Figure 3: GC-SIMDIS Results for 9 cSt, 7 cSt and 5 cSt oil with their used version

In this study, temperature increasing effect has been came to the forefront. Pressure change effect over the chain breaking was less effective considering refrigerant compressor oils.

3.3. ICP-MS Results

In this study, pre-digestion method has been used for the analyzing the inorganic content of the oils. L.M. Costa et al. mentioned that the assurance of metals in oils can be carried out after weakening with natural solvents, or after ashing and/or absorption of the tests with acids. (Costa, 2001).

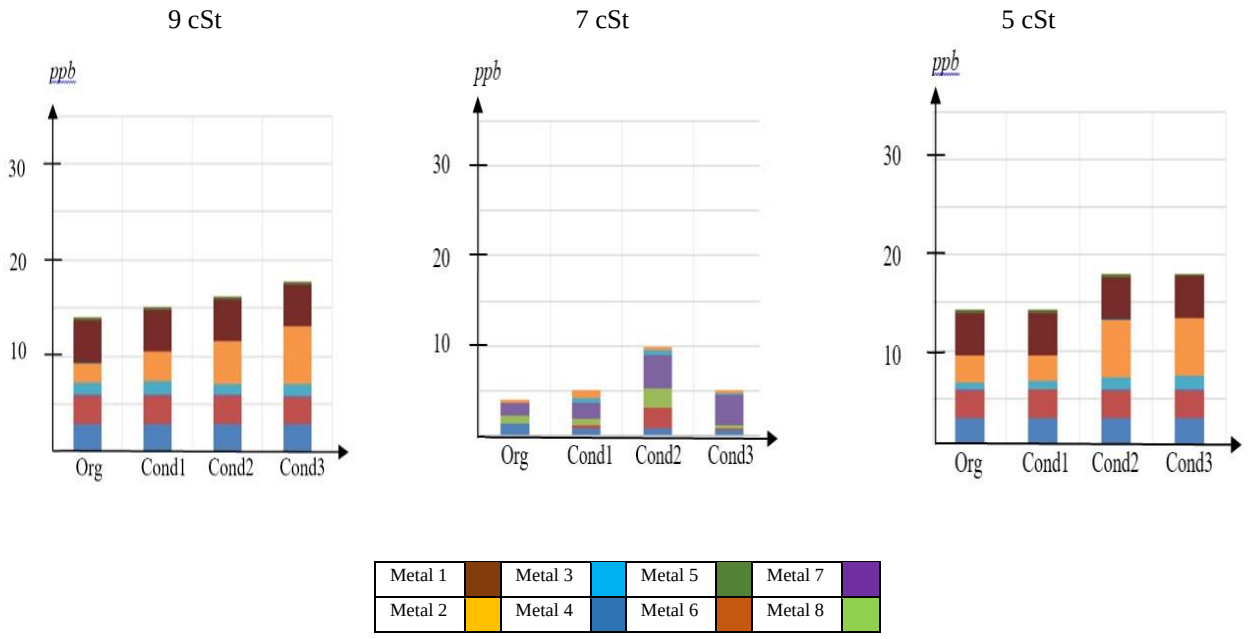


Figure 4: ICP-MS metalic contents results

In Figure 4, 9 cSt, 7 cSt and 5 cSt oils analysis results have been determined respectively. In the analysis, comparison of metallic contents of original and their used oil versions with the 3 different conditions can be seen. Used oil conditions determined regarding the experiment parameters.

4. CONCLUSION

In this study, 3 different refrigerator compressor oil have been analyzed. Their chemical compositions and viscosities were selected as differently. Their unused versions were characterized with the GC-MS and GC-SIMDIS for the organic contents. Also for inorganic contents ICP-MS method has been used. Temperature and pressure were the main gradient for the comparison.

Analysis has been carried out with based on the comparison between the original oils and used oils. These used oils have prepared with applying the 3 determined test conditions regarding temperature and pressure.

For inorganic content, it has been seen that the change between used oils and the original oils did not show significant differences. However, for organic contents, changing of chemical structures and the viscosities, oxidation effects and also variation of the carbon chains have been detected over the GC test results. Regarding these results temperature came frontier compared to the pressure effect for the refrigerator compressor oils that has been selected for this analysis.

These results connected the wearing characteristic of the compressors metallic parts and the lubrication oil which have different chemical compositon and the viscosities. By looking at the analysis, the more defected used oil resulted the wearing for working parts of the compressors, also the more stable chemical composition between used oil and unused oil has showed no wearing characteristic.

For future analysis, the analysis can be carried out with the GCxGC analysis technics or with the HPLC technics based on their more qualified methods. Connection between the organic content changes and the wearing properties is directly depend on each other. Any other analysis technics can be applied for this purpose.

NOMENCLATURE

Symbols

GC	Gas Chromatography	CS_2	Carbon disulfide
MS	Mass Spectroscopy	H_2O_2	Hydrogen Peroksite
SIMDIS	SimulatedDistillation	HNO_3	Nitric Acid
FID	Flame Ionization Detector	Ar	Argon
ICP	InductivelyCoupled Plasma	He	Helyum
M	Molecule	µ	Mikro
e	Electron	ml	Milliliter
eV	Electron Volt	G	Gram
Mo	Mineral Oil	%	Percent
M	Molecule	Ppb	Parts per Billion
		T	Temperature (˚C)

REFERENCES

Bauwens, G., Panto, S., Purcaro, G. (2021) Mineral Oil saturated and aromatic hydrocarbons quantification: Mono- and two-dimensional approaches

Costa, L.M., Silva, F.V., Gouveia S.T., Nogueira, A.R.A., Nobrega, J.A. (2001) Focused microwave-assisted acid digestion of oils: an evaluation of the residual carbon content.

Fujinary, E. M., (1998). 'Chemiluminescent nitrojen detectors (CLND) for GC, SimDis, SFC, HPLC and SEC Applications. Industrum Methods Food Beverage Anal, 39, 376-378.

Greye, J. (2016) Development of Analysis Method for Determination of Mineral Oil Contamination in Cardboard. *Master's Thesis. University of Jyvaskyla*

He, M., Yang, C., Geng, R., Zhao, X., Hong, L., Piao, X., Chen, T., Quinto, M., Li, D. (2015). 'Monitoring of phthalates in foodstuffs using gas pmicrosyringe extraction coupled with GC-MS' Analytica chimica acta 879, 63-65.

Holweger, W. (2013) Fundamentals of Lubricants and Lubrication. Chapter : 'Introduction' http://dx.doi.org/10.5772/55731

Krasomonski, W., Krasodomski, M. (2010). GC/MS Application in the structural group analysis of basic lubricant oils. Part I – State of Knowledge

Mang, T. (2007) Lubricants and their markets. In : Wang, T., Dressel, W.(Eds.), Lubricants and Lubrication. Second ed. Wiley, Verlag GmbH &Co, Weinheim, pp 1-6

Muller, E., Souza, J.P., Muller, C.C., Muller, A.L., Mello, P.A., Bizzi, C.A. (2016) Microwave-assisted wet digestion with H_2O_2 at high temperature and pressure using single reaction chamber for elemental determination in milk powder by ICP-OES and ICP-MS. Talanta, 156, 232-238

Telgmann, L., Lindner, U., Lingott, J., Jakubowski, N. (2016) Analysis and Speciation of Lanthanoides by ICP-MS. Journal Physical Sciences Rewievs http://doi.org/10.1515/psr-2016-0058

Wilke, J., Kryk, H., Hartmann, J., Wagner, D. (n.d.) Theory and Praxis of Capillary Viscometry

Yücel, H. G. (2005) Prediction of molecular weight and density of n-alkanes(C6-C44). Analytica chimica acta, 547(1), 94-97