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Review paper

THE ROLE AND IMPORTANCE OF CHROMATOGRAPHY AND SPECTROSCOPY IN THE ANALYSIS OF NONCONVENTIONAL FUELS

Abstract

Nonconventional fuels are gaining in importance due to limited availability of crude oil and rapid growth of the automotive industry and transportation sector which is resulting in increased emissions into the environment. Exhaust gases associated with combustion of fossil fuels used in transportation sector reduce air quality and thus have direct impact on human health. Biofuels are more environmentally friendly alternative fuels that are produced from animal or vegetable feedstocks. Developments of new and more effective analytical methods are increasing since the knowledge of the chemical composition represents challenge to analysts. In this paper, the most common and important chromatographic and spectroscopic methods in the analysis of feedstocks and nonconventional fuels are shown. The paper also presents the characteristic chromatogram and spectra of certain feedstocks for biofuel production and chromatogram of biodiesel recorded in the Laboratory for testing, water, hydrocarbons and materials (Central Testing Laboratory Department) in INA Petroleum Industry.

Key words: *nonconventional fuels, NMR spectroscopy, gas chromatography, liquid chromatography*

1. INTRODUCTION

In the last decade, environmental, economic and social interest in using of nonconventional fuels such as bio-oils, oil sands bitumen and coal pyrolysis oils has increased rapidly.[1] The petroleum market instability, limited availability of crude oil, and negative impact of the use of fossil fuels on the environment have currently stimulated the spread of alternative fuels.[2] Therefore, considerable efforts and resources are invested in the development of energy production from renewable sources. Renewable energy effectively uses natural resources by technologies range from solar power, wind power, hydroelectricity/micro hydro, biomass and biofuels for transportation; the term biomass in particular include organic animal and vegetal provenance materials that could be utilized for energetic and compost aims.[3]

Biomass is a renewable energy source and an alternative to fossil fuels. Depending on the type of biomass biofuels are categorized as first, second and third generation. In recent years, animal fats and used vegetable oils are increasingly being used as feedstock for biodiesel production. Furthermore, lipids isolated from algal biomass can also be used as feedstock for biodiesel production.

Most of what is known about alternative fuels chemistry today results from the use of highly sophisticated spectroscopic and chromatographic methods. Chromatography is able to provide the capability to gain a detailed understanding of the chemical composition and trace contaminant content for volatile and nonvolatile samples, while spectroscopy can be used to provide quick answers on final product quality. This paper will present the role and importance of nuclear magnetic resonance (NMR) spectroscopy, and gas (GC) and high performance liquid (HPLC) chromatography in the analysis of nonconventional fuels.

2. OVERVIEW

2.1 NMR spectroscopy

NMR spectroscopy is a technique which is more and more being used for characterization, structural and compositional analysis of nonconventional oils. [1,4,5] It has many advantages over routine chromatography and mass spectrometry methods such as simple sample preparation, faster analysis and use of small amount of solvents which is environmentally acceptable. NMR can be applied to analyze biodiesel, diesel and biodiesel mixtures and it can provide detailed molecular information.[6-10] ¹H NMR spectroscopy has been frequently used for the quantitative and qualitative analysis of vegetable oils, animal fats and their derivatives.[11]

The group of authors investigated the fatty acid profile by ¹H NMR spectroscopy and elaborated a method for quantification of fatty acids in the mixture. The method was applied to mixtures containing the triacylglycerol or alkyl esters of palmitic, stearic, oleic, linoleic and linoleic acids and it could theoretically be applied to oils or fats containing other fatty acids.[5] Biodiesel is basically composed of fatty acid methyl esters (FAME). A typical ¹H NMR spectrum of fatty acid methyl esters is displayed in the Figure 1. Physical properties of biodiesel are very similar to fossil diesel and it can be used pure or mixed with fossil diesel. NMR spectroscopy in combination with principal component analysis (PCA) has been shown to be a powerful tool for determining biodiesel present in blends and in identifying the biodiesel sources.[1] M. Oromi-Farrus and coworkers analyzed iodine values of biodiesel samples with 1,4-dioxane as an internal standard using ¹H NMR spectroscopy and standard iodometric method.[12] The obtained results were compared to those determined by the standard method and good correlation was observed. The use of internal standard allows for a direct determination of iodine value of biodiesel samples. The iodine value parameter represents the total degree of unsaturation in vegetable oils and fats.

Determination of the iodine value is very important because high iodine value can cause serious problems including formation of various degradation products that is related to engine problems.

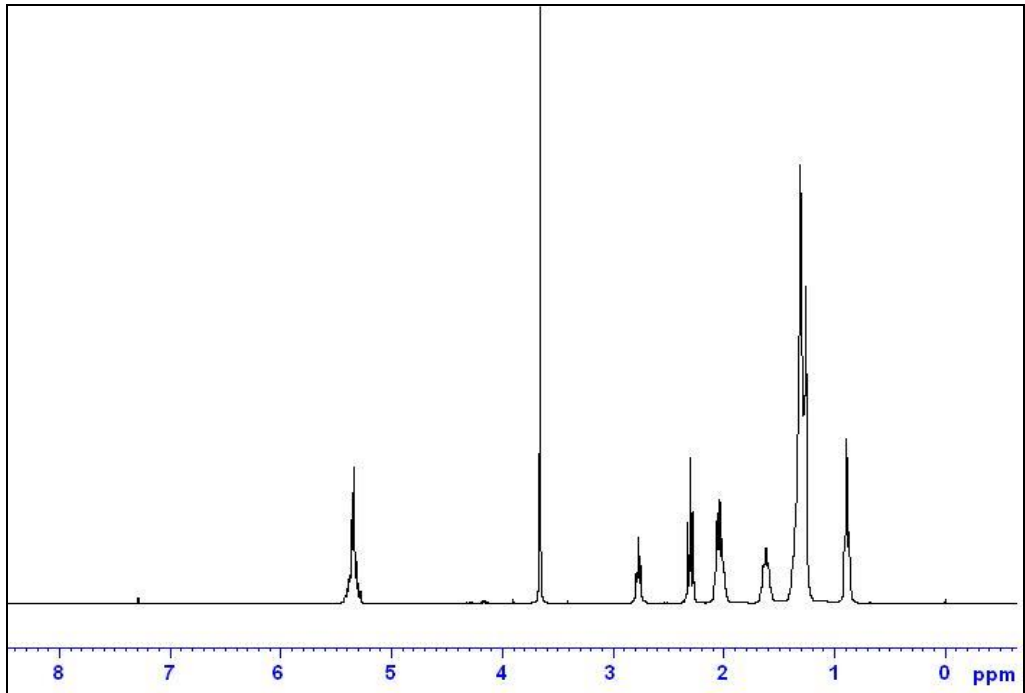


Figure 1: Typical ^1H NMR spectra of fatty acid methyl esters

The biodiesel has a few disadvantages over fossil diesel such as oxidative stability. Many factors influence the oxidative stability of biodiesel. It has been reported that the oxidative stability is a critical issue in production and use of biodiesel because it affects the quality of the fuel.[13] G. Knothe explored the possibilities of NMR techniques to analyze oxidized biodiesel and the effect of contact area with air. The results showed that increasing surface area accelerated oxidation and affected fatty acid composition. ^{13}C NMR spectroscopy was applied to determine fatty acid distribution in triacylglycerols of vegetable oils with high-low oleic and high linolenic acid.[14] Also, 1D and 2D NMR spectroscopy has been applied to monitor the transesterification reaction.[15] ^1H NMR DOSY methods were used to examine acylglycerols and fatty acid methyl ester.[16] This technique relies on translational diffusion and can be used to identify different compounds present in the complex sample according to their differences in diffusion properties. It can provide information about the size and shape of each compound present in the mixture.

Furthermore, it has been reported that NMR spectroscopy can be used for estimation of free fatty acid content in oils, fats and biodiesel and has been found to be more accurate than the conventional titrimetric analysis for the estimation of FFA content. This method can be used for to monitoring esterification reaction of FFA to biodiesel.[16] The necessity to reduce greenhouse gas emissions has increased interest in lignocellulose. Solid state CP/MAS ^{13}C NMR spectroscopy has been proven useful and powerful tool for characterization of lignin, cellulose and hemicellulose. It is a promising technique for the analysis of biomass polymers.[17,18] A typical ^{13}C CP/MAS NMR spectrum of cellulose is displayed in the Figure 2.

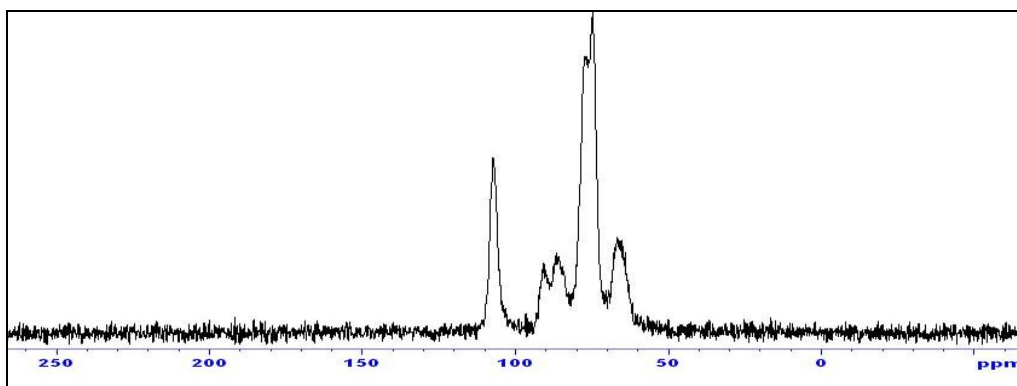


Figure 2: Typical ^{13}C CP/MAS NMR spectra of cellulose

2.2 GC

Gas chromatography is very important technique in analysis of fats and oils because accurate results can be obtained for complex, as well as simple samples. In gas chromatography free fatty acids show tailing, so transformation to fatty acids methyl esters is necessary. Lipids are extracted from matrices using a non-polar solvent, such as ethers, and are saponified to produce the free fatty acid salts. The fatty acid salts then are derivatized to form the fatty acid methyl esters, to increase volatility, improve peak symmetry, and decrease sample activity, thus providing more accurate analytical data. The derivatization method does not alter the fatty acid composition of the feedstock; the composition of FAME is assumed to be the same as the composition of fatty acids in feedstock. Lipids can be determined as FAME after direct, *in situ* transesterification of algal biomass with an acid catalyst – hydrochloric acid in methanol.[19] Lipids as total FAME are calculated from the sum of the FAME concentration determined by GC. The most important parameters of biodiesel such as fatty mono-alkyl esters, fatty acids, glycerol and their acyl derivatives are commonly determined by gas chromatography. In fact, GC has been the most used technique due to its high accuracy for the quantification of minor components.

Flame ionization detection is the most widespread detector used in GC, but the utilization of mass spectrometer has increased. The relative amounts of FAME in biodiesel can vary widely and have different effects on the fuel properties.[20] FAME analysis is carried out with split injection onto a capillary column with polar stationary phase and an a FID detector. Analysis is based on sample preparation with internal standard with precise mass, methyl nonadecanoate.

Glycerol is the major by-product in the manufacturing of biodiesel. Its removal is desirable since it can cause damage to the engine and hazardous emissions. As a consequence, quality control of this compound is essential.[21] European standards specify the tolerable limits of free and total glycerol. Since the limits of total and free glycerol are very low, there is a need for precise and reliable analytical methods for both compounds.[22] Only GC meets all requirements for the determination of low content of mono-, di- and tryglycerides in biodiesel. The determination of all classes of compounds was achieved by the silylation of the free hydroxyl groups, employing N-methyl-N-trimethyl-silyl-trifluoro-acetamide, MSTFA. The use of internal standards, 1,2,4-butanetriol for determining glycerol and 1-glyceryl-monononadecanoate, 1-3-glyceryl-dinonadecanoate and glyceryl-trinonadecanoate for determining glycerides provides reliable quantitative gas chromatography analysis within a run time of approximately 30 minutes (Figure 3).

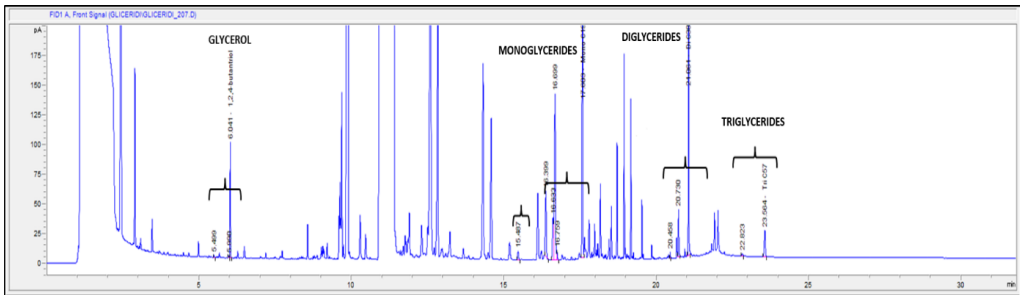


Figure 3: Chromatogram of biodiesel analysis for determining mono-, di-, triglycerides, free and total glycerol

The residual methanol in biodiesel can cause corrosion of metals, mainly of aluminium and decrease the biodiesel flash point. Besides, it is responsible for cetane number and lubricity decreasing of fuel. GC analysis for determining methanol content in biodiesel involves headspace sample preparation with internal standard with precise mass, isopropanol (Figure 4).

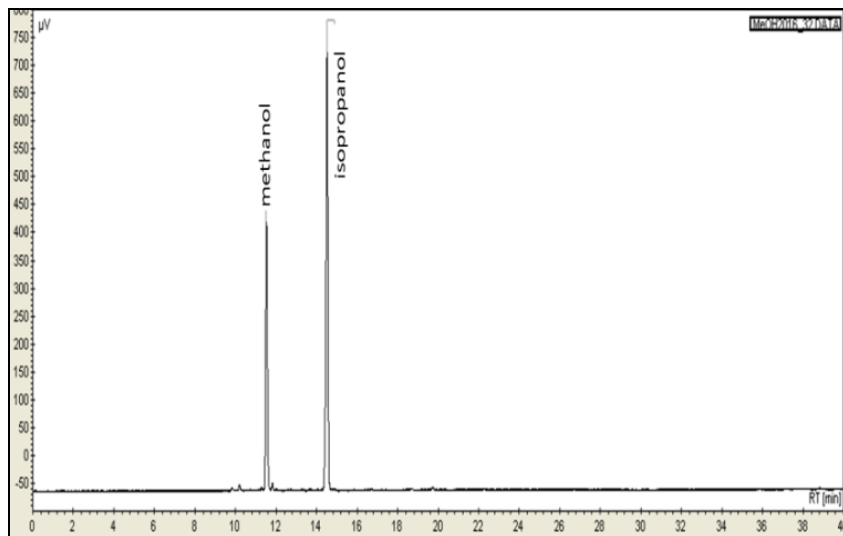


Figure 4: Chromatogram of biodiesel analysis for determining methanol

Bioethanol is an alcohol made by fermentation, which can be used as fuel in its pure form, but is more commonly used as a gasoline additive to increase octane and improve vehicle emissions. The presence of by-products in the bioethanol can decrease the purity of the bioethanol itself. Some of the impurities are not allowed in the product, such as methanol.

The qualitative and quantitative analysis of organic impurities can be carried out by using GC-FID on suitable capillary column. Some of impurities that can be quantified are: methanol, butanol, propanol, isobutanol, 3-methylbutanol, 2-methylbutanol, acetal, acetaldehyd, etil acetat. Technique also provides information about ethanol content.

2.3 HPLC

High performance liquid chromatography (HPLC) is widely applied in the analysis of crude oil, petroleum distillates and commercial petroleum products. The development of non-conventional fuels from various origins is connected with the development of new chromatographic methods and improvement of existing ones. HPLC analysis of petroleum products includes separation and identification according to group hydrocarbon composition, as well as the separation, identification and quantification of target components. Different HPLC types involving the use of various chromatographic columns with a polar, non-polar stationary phases or ion exchangers, different mobile phase compositions and the detection systems enable analysis of samples of different physical and chemical characteristics, solubility, density and polarity.

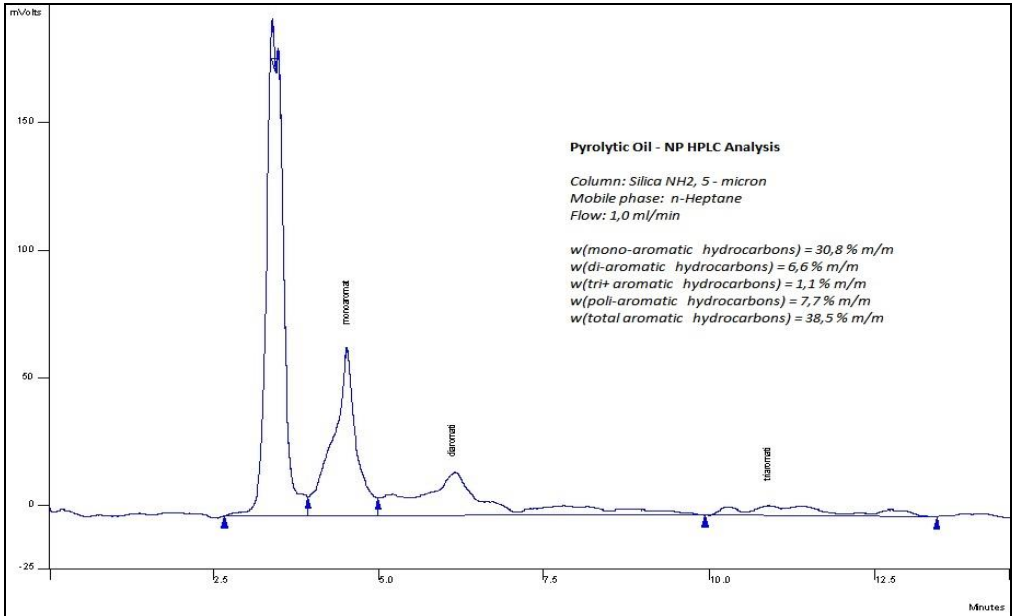


Figure 5: NP-HPLC analysis of pyrolytic oil

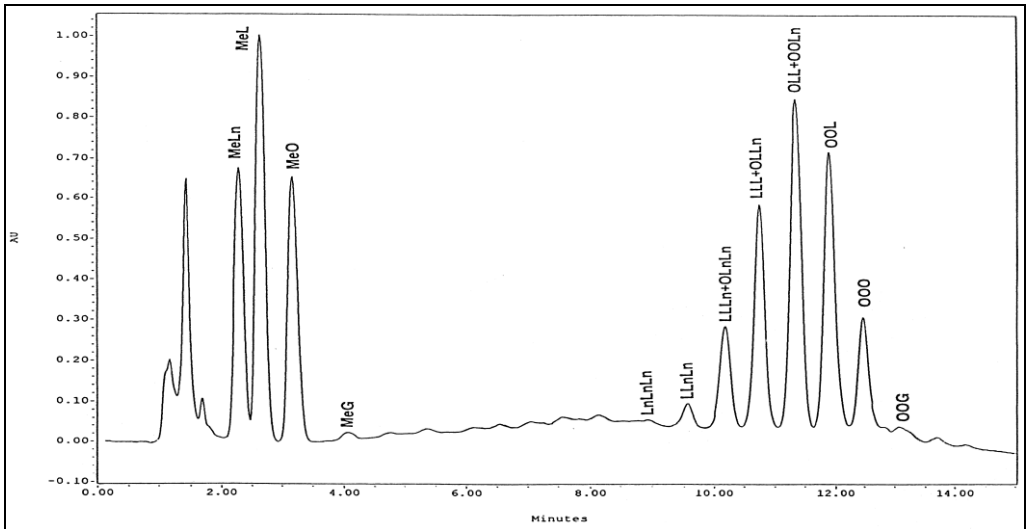


Figure 6: HPLC separation of a mixture of rapeseed oil and biodiesel

Normal phase liquid chromatography (NP-HPLC) used in the analysis of organic samples has found wide application in determining the content of aromatic hydrocarbons in the middle oil distillates.[23] By adding bio-components of various origins to diesel fuel, its aromatic hydrocarbon content is being considerably lowered. Monitoring content of poly-aromatic hydrocarbons (PAH) is especially significant since they are legally limited to a maximum 8 %m/m. Monitoring of hydrotreated vegetable oil (HVO) as a bio-component in diesel fuel is described in the literature while aromatic content is being determined in raw materials and after blending.[24] Also, NP-HPLC is used for monitoring hydrocarbon composition of the mixture formed by blending pyrolytic oils obtained from used car tires in diesel fuel.[25] Figure 5 shows the HPLC chromatogram of pyrolytic oil.

Reverse phase liquid chromatography (RP-HPLC) is used for the analysis of water-soluble samples. It has been applied in the analysis of biomass used in the production of biofuels.[26] There are three main constituents of plant biomass: cellulose, hemicellulose and lignin. By biomass hydrolysis polymeric carbohydrates are hydrolyzed into the monomeric form, which are soluble in aqueous solutions and as such can be analyzed on the HPLC with the refraction index detector. Gradient elution RP-HPLC was used for the determination of compounds occurring during the production of biodiesel from rapeseed oil.[27] Figure 6 shows chromatographic separation of a mixture of rapeseed oil and biodiesel.

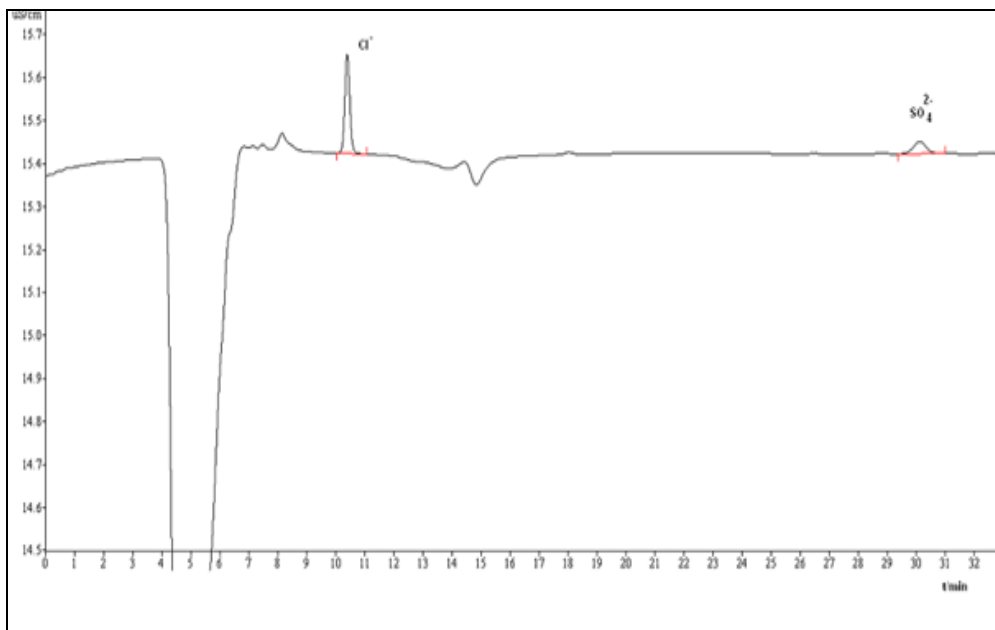


Figure 7: Ion chromatographic analysis of bio-ethanol

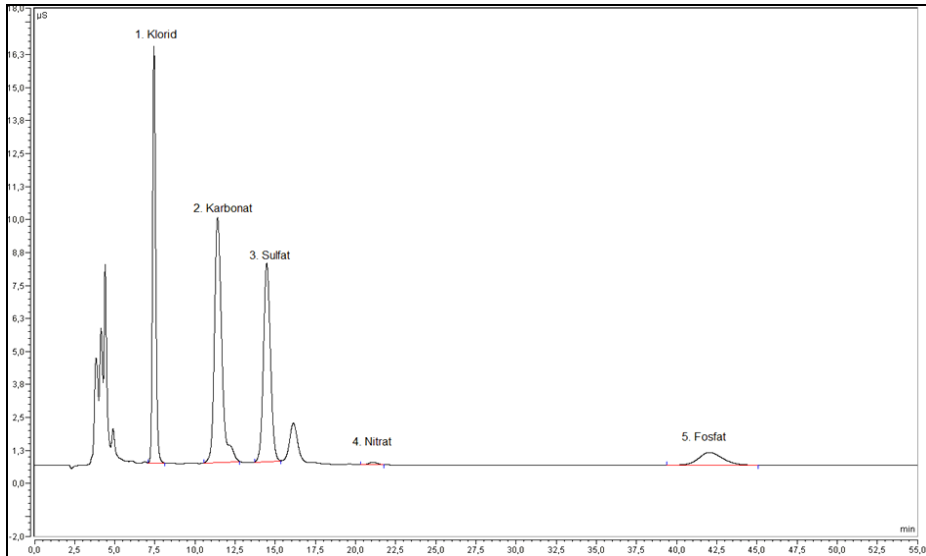


Figure 8: Ion chromatographic analysis of Miscanthus aqueous solution, anion separation

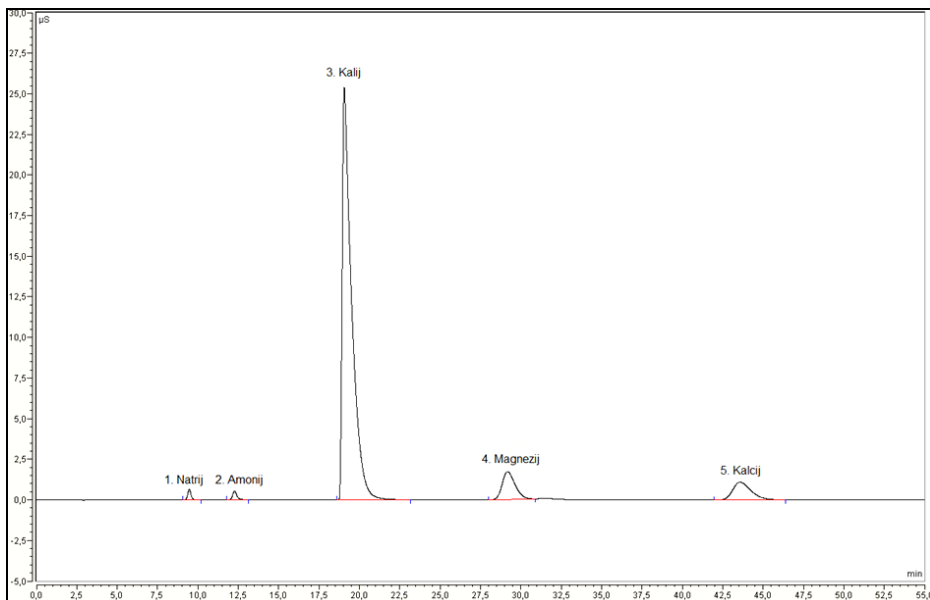


Figure 9: Ion chromatographic analysis of Miscanthus aqueous solution, cation separation

Ion chromatography with conductivity detection is a standardized method for determining chloride and sulfate in bio-ethanol (Figure 7) produced from biomass or biodegradable waste. Bio-ethanol is used as a blending component in commercial gasoline.[28] Content of chloride and sulfate in ethanol is monitored because of their influence on the system corrosion and formation of the deposits.

Ion chromatography is used in determination of the content of water-soluble chloride, sodium and potassium in solid biofuels (Figures 8 and 9). Combustion of biomass leads to the formation of ash whose ingredients including chloride, sodium and potassium. Ash melting may cause the formation of sediment and pollution in engines.

3. CONCLUSIONS

Methods described in this overview are suitable for analyses of all types of non-conventional fuels and feedstocks they are produced from. The examples presented in this paper show a great potential of these methods.

Owing to the fact that these techniques are in constant development, theoretical and instrumental, more applications are expected in the future.

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