

CHARACTERIZATION OF IONS IN BIO-ETHANOL USED FOR BIO-FUEL BLENDING

TATJANA TOMIĆ, MARTINA MILČIĆ¹, NADA UZORINAC NASIPAK, SANDRA BABIĆ¹

INA – Industrija nafte d.d., Product Development Department, Central Testing Laboratory, Zagreb, Croatia

¹Faculty of Chemical Engineering and Technology, University of Zagreb, Croatia
e-mail: tatjana.tomic@ina.hr

The development and widespread use of bio-fuels require the development of appropriate analytical procedures and methods to monitor their composition and properties either as single raw material or as parts of mixed commercial product. Bio-ethanol is ethanol produced from biomass or biodegradable waste and used as a blending component in commercial gasoline fuel. Bio-ethanol can be contaminated with chloride and sulfate ions which can cause various unwanted side effects like corrosion and forming deposits. European norm, EN 15376 defines the maximum permitted level of ions present and by that maximum chloride and sulfate content should not exceed 6.0 mg·kg⁻¹ and 4.0 mg·kg⁻¹, respectively. In this paper, the applicability of the ion chromatography method for chloride and sulfate determination in bio-ethanol with satisfactory precision, simple sample preparation and short analysis time is shown.

Key words: bio-ethanol, chloride, sulfate, ion chromatography.

Karakterizacija iona u bio-etanolu koji se koristi za umiješavanje u bio-gorivo. Razvoj i sve šira upotreba bio-goriva zahtijevaju razvoj odgovarajućih analitičkih postupaka i metoda za praćenje sastava i svojstava bio-goriva, bilo kao pojedinačne sirovine ili kao komponente konačnog komercijalnog proizvoda. Bio-etanol je etanol proizveden iz biomase ili biorazgradivog otpada i koristi se kao komponenta za umiješavanje u komercijalni benzin. Bio-etanol može biti kontaminiran kloridnim i sulfatnim ionima koji mogu izazvati različite neželjene nuspojave poput korozije i stvaranja taloga. Europski standard EN 15376 definira maksimalno dopušten sadržaj prisutnih iona u bio-etanolu i on za kloride iznosi 6,0 mg · kg⁻¹, a za sulfate 4,0 mg · kg⁻¹. U ovom radu prikazana je mogućnost primjene metode ionske kromatografije pri određivanju klorida i sulfata u bio-etanolu uz zadovoljavajuću preciznost, jednostavnu pripremu uzoraka i kratko vrijeme trajanja analize.

Ključne riječi: bio-etanol, klorid, sulfat, ionska kromatografija.

INTRODUCTION

Environmental awareness and ecological demands introduce a wide use of different bio-fuels. Replacement of regular fuels by bio-ethanol blended fuels is endorsed and favored worldwide. Ethanol is one of the main components for future reformulated fuels and offers great advantages due to its physical-chemical

characteristic, raw materials availability, low production costs and beneficial environmental effects [1]. It can be used in petrol engines as a replacement for gasoline; it can be mixed with gasoline to any percentage. Bio-ethanol is produced from biomass by the fermentation of sugar-containing plants such as sugar cane or corn and it is a renewable

source of energy, unlike fossil fuels whose reserves are limited. Bio-mass is the biodegradable fraction of products, waste and residues from agriculture, forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste [2]. From an environmental standpoint bioethanol as fuel has significant advantages over fossil fuels. Many benefits are achieved by replacing conventional fuel additives with ethanol eg. in the reformulated gasoline, bioethanol replaces additives which serve to increase the octane number such as tetraethyl-lead, benzene or MTBE (methyl tetra butyl ether), which all are toxic and pollute air and water. The combustion of bio-ethanol is cleaner than combustion of gasoline and presents less danger of causing fire than gasoline. A great advantage of bioethanol use is in reducing the amount of greenhouse gases. The problem of using ethanol as a component of gasoline is due to incompatibility with the materials that are used in the engines, which are compatible with regular gasoline. Bio-ethanol added to bio-fuels may contain certain content of different ions. Some of the ions present need to be monitored due to possible problems they can create. Chloride and sulfate are ions which can cause various unwanted side effects like corrosion and forming deposits [3, 4]. The maximum allowed level of chloride content in bio-ethanol is the $6 \text{ mg}\cdot\text{kg}^{-1}$ and sulfate $4 \text{ mg}\cdot\text{kg}^{-1}$ [5].

In the literature different methods have been described for the analysis of inorganic ions in such matrix: wet chemical methods such as colorimetry, gravimetry and titrimetry, electrochemical techniques such

as use of an ion-selective electrode and amperometric titrations but many of these methods suffer from interferences, limited sensitivity and time consumption; they are often difficult to automate. Method for determination of chloride and sulfate in the bio-ethanol by X-ray fluorescence after a precipitation procedure was also described [6].

For multiple ions determination use of several different methods is often required. For such determination ion chromatography (IC) is favorable by European norms EN 15376 and EN 15492 [7] and defined as the standard method for the determination of chloride and sulfate ions in bio-ethanol using aqueous sample injection. In this paper ion chromatographic determination of chloride and sulfate, in bio-ethanol samples is presented. The possibility of analysis of bio-ethanol by direct injection of the sample onto the ion chromatographic column without tedious sample preparation step was investigated. Ion chromatography is an analytical technique that separates ions from sample based on their affinity to the ion exchanger. Anion separations use dilute bases, most commonly hydroxide or carbonate, as mobile phases on polymer-based anion-exchange stationary phases. Conductivity detection used in this work is by far the most commonly employed mode of detection in IC. The conductivity detector is a bulk property detector that measures the conductivity of the mobile phase. In a conductivity detector, the resistance (or strictly the impedance) between two electrodes in the flow cell is measured.

EXPERIMENTAL

Materials

As mobile phase in the system, mixture of sodium carbonate, Na_2CO_3 (Kemika, Zagreb, Croatia) and sodium hydrogencarbonate, NaHCO_3 (Merck, Darmstadt, Germany) of chromatographic purity in deionised water (18 M Ω) obtained from TKA Pacific/Gen Pure water purification system (TKA Water Purification Systems GmbH, Germany) has been used. For chemical suppressor regeneration

sulfuric acid (H_2SO_4), p.a. (Kemika, Zagreb, Croatia) has been used. For calibration purpose commercial chloride and sulfate standard solutions were used with concentration of 30 $\text{mg}\cdot\text{L}^{-1}$ and 150 $\text{mg}\cdot\text{L}^{-1}$ (Dionex, USA), respectively. Standard stock solutions were diluted to appropriate concentrations with deionized water and calibration curves were constructed.

Experimental condition

Ion chromatography system (Metrohm IC 761, Switzerland) used for analysis is a complex modular system consisting of the injection system (766 IC Sample Processor, Metrohm, Switzerland), high pressure pump with flow rate ranged from 0.2 $\text{mL}\cdot\text{min}^{-1}$ to 2.5 $\text{mL}\cdot\text{min}^{-1}$ and maximum pressure of 15 MPa, peristaltic pump used for suppressor regeneration, tanks with solvents ($\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ mobile phase, H_2SO_4 for suppressor regeneration, deionized water for system purification), conductivity detector, chemical suppressor (100 $\text{mmol}\cdot\text{L}^{-1}$ H_2SO_4 at flow of 0.6 $\text{mL}\cdot\text{min}^{-1}$ and deionized water at same flow rate were used for suppressor regeneration) and chromatographic column Metrosep A Supp 5/250 (250 x 4.0 mm I.D.). The column has carrier material polyvinyl alcohol with quaternary ammonium groups and particle size of 5 μm . In a system for ion chromatography there is also suppressor module included when the conductivity

detectors are used and the mobile phase is intensively conducting, saturating the detector's response. Injection volume was 20 μL . Chromatographic system is completely controlled by the Methrom IC Net 2.1 program. The same computer program collects and processes analytical data. Ion chromatograph has been prepared by including all individual modules of the instrument and computer software to the computer. The solvent tank was filled with mobile phase and purge for 5 minutes. Run flow rate was set at 0.5 $\text{mL}\cdot\text{min}^{-1}$ and then after 20 minutes gradually increasing to the working flow rate of 0.6 $\text{mL}\cdot\text{min}^{-1}$. After stabilization of the flow, pressure and detector, the instrument is ready for the operation. The samples of bio-ethanol were filtered before analysis through a regenerated cellulose membrane filter with pore size of 0.45 μm to remove undissolved particles from the sample. Volume of injected sample was 20 μL .

RESULTS AND DISCUSSION

The paper describes the analysis of bio-ethanol used as bio-fuel component in terms of the chloride and sulfate content

determination by ion chromatography. Ion chromatography method suitable for simultaneously determination of chloride

and sulfate ions in bio-ethanol at low concentration levels avoiding laborous sample preparation and with good accuracy. The analysis requires a small amount of the test sample, and the duration of the analysis is relatively short. A mixture of sodium carbonate and sodium bicarbonate ($\text{Na}_2\text{CO}_3/\text{NaHCO}_3$) was used as the mobile phase. Retention of specific ions on the chromatographic column with a mobile phase flow rate of $0.6 \text{ mL}\cdot\text{min}^{-1}$ was

Calibration

The calibration is performed by means of external standard method at the $0.6 \text{ mL}\cdot\text{min}^{-1}$ flow rate and carbonate / bicarbonate mobile phase. The external

monitored. It was noted that the time between negative peak and chloride ion peak is getting longer at flow rate of $0.6 \text{ mL}\cdot\text{min}^{-1}$, than in the case of higher mobile phase flow rates, while the total analysis time was a little longer. Extended time between negative peak and chloride ion peak is desirable from the analytical point of view because of the potential overlap and overlay of chromatographic peaks that can occur in real samples.

calibration is the most commonly used calibration method meaning that calibration standards are prepared and analyzed separately from the samples.

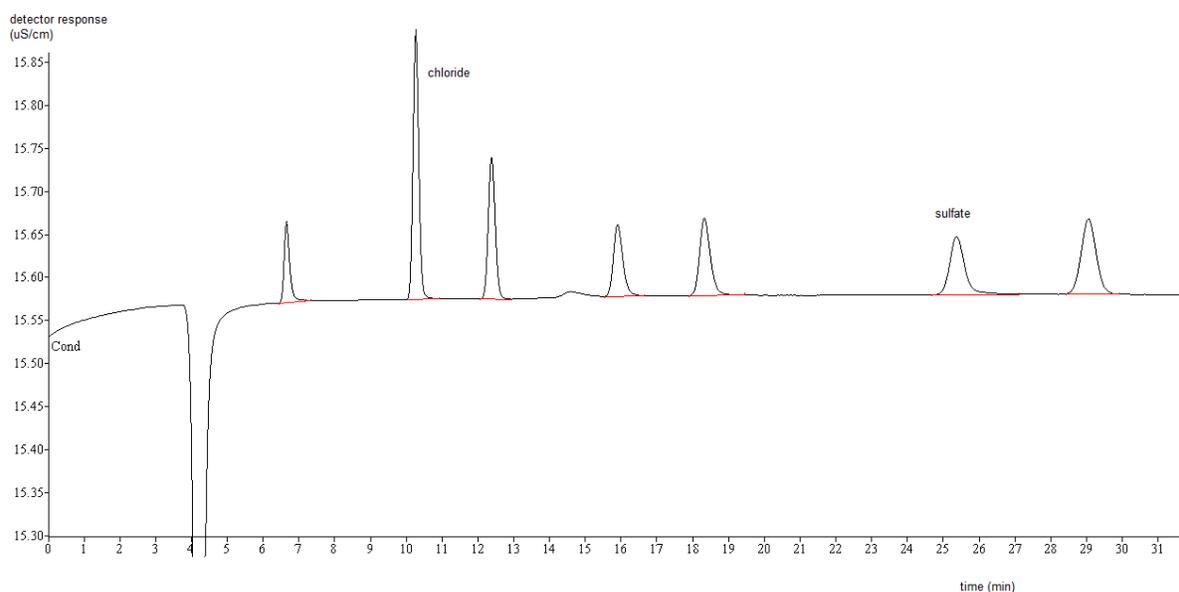


Figure 1. The chromatogram of the calibration standard

Slika 1. Kromatogram kalibracijskog standarda

Calibration curves were prepared by plotting the peak area versus the analyte concentration expressed in $\text{mg}\cdot\text{L}^{-1}$. By means of calibration curves, individual ions are quantified as mass concentration. Each standard was measured in triplicate in seven

calibration points in concentration range from $0.25 \text{ mg}\cdot\text{L}^{-1}$ to $20 \text{ mg}\cdot\text{L}^{-1}$ for both ions. From Figures 1 and 2 it can be seen that good linearity was achieved with the correlation coefficients greater than 0.999 for both calibration curves.

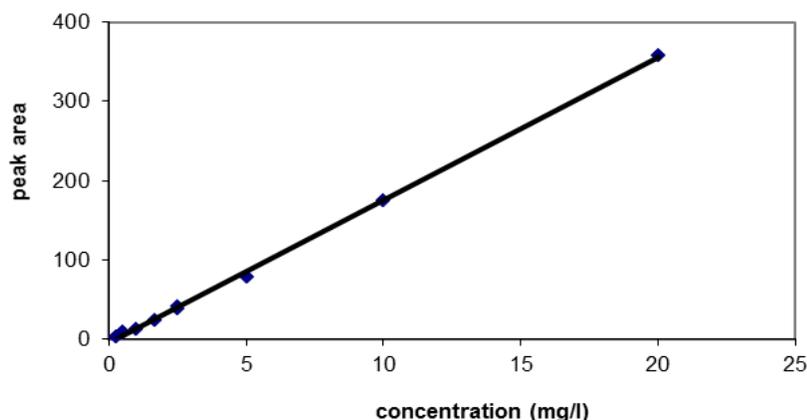


Figure 2. Calibration curve of chloride, the correlation coefficient $R^2=0.9997$
Slika 2. Kalibracijska krivulja klorida, koeficijent korelacije $R^2=0.9997$

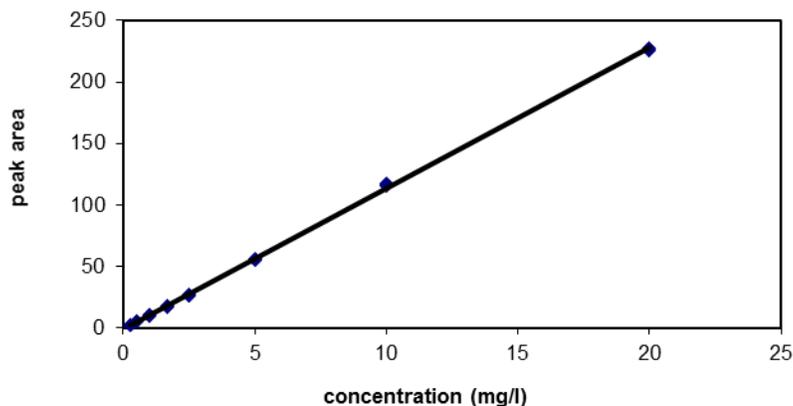


Figure 3. Calibration curve of sulfate, the correlation coefficient $R^2=0.9999$
Slika 3. Kalibracijska krivulja sulfata, koeficijent korelacije $R^2=0.9999$

After calibration, precision of the method was evaluated by determining the repeatability. The method repeatability was evaluated by injecting by measuring the chloride and sulfate contents in a corresponding sample six consecutive times under identical conditions and performed by the same operator in the laboratory.

Repeatability was expressed as means of percentage of relative standard deviations (% RSD). For chloride repeatability was 0,9 % while for sulfate repeatability was 3,2 %. As in all cases the RSD values are lower than the accepted value of 5 % and the method is considered repeatable.

Quantitative analysis of the chloride and sulfate ions in bio-ethanol samples

In four real bioethanol samples used as the components for the fuel blending, the content of the present chloride and sulfate

ions was determined. Chromatogram of bio-ethanol sample as representative chromatogram is presented on Figure 4.

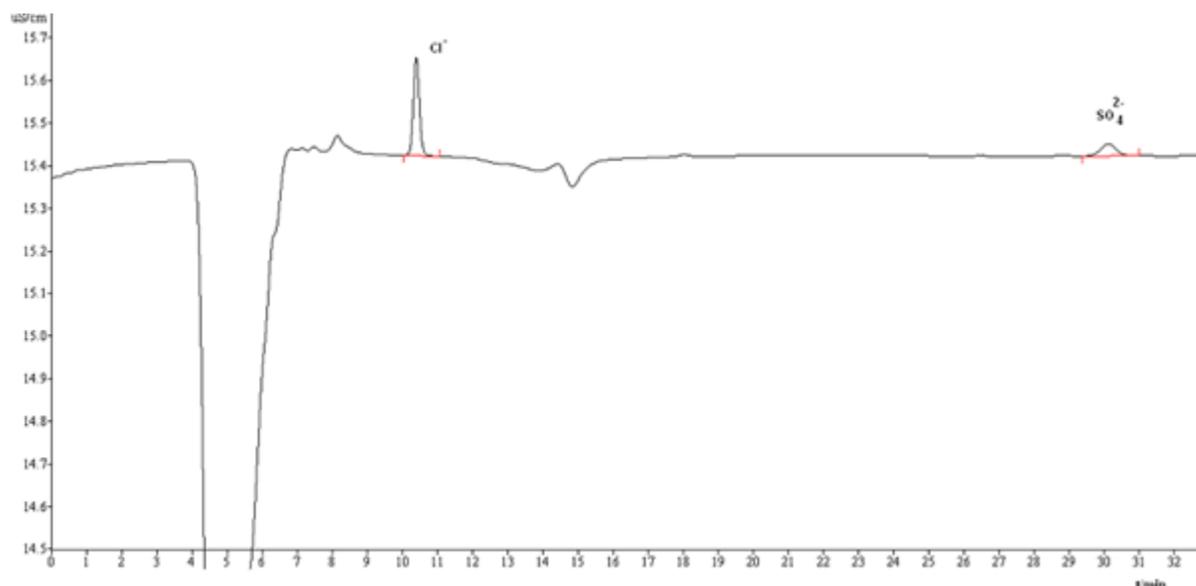


Figure 4. Chromatogram of real bio-ethanol sample
Slika 4. Kromatogram realnog uzorka bio-etanola

Total analysis time was 35 minutes and when analyzing a real sample, the sulfate retention time is slightly longer comparing to standard due to the matrix influence. The content of chloride and sulfate ions in analyzed samples obtained in

units of $\text{mg}\cdot\text{L}^{-1}$ (from calibration curves) were expressed in $\text{mg}\cdot\text{kg}^{-1}$ taking into account density of each bio-ethanol sample. Quantitative results of the chloride and sulfate content determination in the bio-ethanol samples are shown in Table 1.

Table 1. Chloride and sulfate concentrations, w ($\text{mg}\cdot\text{kg}^{-1}$)

Tablica 1. Koncentracije klorida i sulfata, w ($\text{mg}\cdot\text{kg}^{-1}$)

Bio-EtOH sample no.	<i>chloride</i> w ($\text{mg}\cdot\text{kg}^{-1}$)	<i>sulfate</i> w ($\text{mg}\cdot\text{kg}^{-1}$)
1	0.36	0.22
2	0.29	1.26
3	0.29	0.82
4	0.44	0.21

As can be seen from chromatogram in Fig 4. baseline has not been stable at the start of the chromatogram as well as a wide negative peak comes close to chloride peak. Both, chloride and sulfate contents in samples are for a concentration decade smaller than the allowable limits of $6 \text{ mg}\cdot\text{kg}^{-1}$ for chloride and $4 \text{ mg}\cdot\text{kg}^{-1}$ for sulfate. Requirements of EN 15492 method for precision are defined in concentration range from $4 \text{ mg}\cdot\text{L}^{-1}$ to $30 \text{ mg}\cdot\text{L}^{-1}$ while for the lower chloride content there are no data available and therefore cannot be applied. For sulfate content precision was not established yet in EN 15492. For both ions

precision should be determined in much lower range comparing to their content in real samples. On the Croatian market in the plan is the sale of gasoline which contains bio-component and bio-ethanol as a feedstock for their mixing will be routine analyzed in terms of determining the content of chloride and sulfate. Ion chromatography has proven to be a very suitable method for this purpose. Further efforts should be directed to determining the chloride and sulfate content in gasoline containing the bio-component by a method that is fast, precise and requires a small initial sample volume for analysis.

CONCLUSION

Recent introduction of bio-ethanol as a component for the mixing into gasoline requires the development of new fast and reliable analytical methods for the determination of different physical and chemical properties and ionic species present, which may lead to undesirable effects. The results obtained in this work indicate that the proposed ion chromatography method offers adequate solution for chloride and sulfate content determination in bio-ethanol.

The method was found to be precise, rapid and requires a small amount of sample for analysis. Method allows bio-ethanol analysis without previous sample preparation step thus significantly improving sample throughput and reduce sources of possible errors. Results for repeatability show the acceptability of the method to ions determination. Furthermore, the method is able to determine low chloride and sulfate levels expected in real bio-ethanol samples.

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