

Simultaneous quantitative analysis of inorganic anions in commercial waste-oil biodiesel using suppressed ion exchange chromatography

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Ion exchange chromatography was applied to simultaneous quantitative analysis of fluoride, chloride, bromide, nitrate, sulfate and phosphate anions in commercial waste-oil biodiesel. The extraction of the anions was carried out with deionized water using separation funnel. The observed limits of detection in $\mu\text{g}\cdot\text{mL}^{-1}$ were, respectively: fluoride 0.0012; chloride 0.0029; bromide 0.0116; nitrate 0.0089; sulfate 0.0094 and phosphate 0.0267. The observed amounts in $\text{mg}\cdot\text{Kg}^{-1}$ were, respectively: fluoride 1.714; chloride 8; phosphate 0.594; sulfate 1.773. The amounts of bromide and nitrate anions were lower than the limits of detection in all the studied samples and not detected. The method can be considered to be green because it uses small volumes of water, is simple, with fine recovery rates. Anions in biodiesel can be analyzed simultaneously by ion chromatography.

Key words: Ion exchange chromatography, Commercial waste-oil, biodiesel, Quantitative analysis, Inorganic anions, Separation funnel.

INTRODUCTION

Biodiesel is made from a diverse mix of feedstocks including recycled cooking oil, soybean oil and animal fats through a chemical process called transesterification. Biodiesel that meets strict technical fuel quality and engine performance specifications. Tests had shown that the addition of a small amount of biodiesel to diesel can significantly increase the lubricity of the fuel in short term [1]. However, over a longer period of time, studies showed that biodiesel loses its lubricity [2]. This could be because of corrosion over time due to oxidation of these anions.

Recently, G. Dugo et al. quantified the F^- , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and I^- in commercial seed oils and virgin olive oils produced from de-stoned olives using suppressed ion exchange chromatography [3]. E.L.C. Silveira et al. determined simultaneously the acetate, formate, chloride, phosphate, and sulfate anions in biodiesel by ion chromatography, the extraction of the anions from the matrixes was performed using water with the assistance of ultrasound [4]. L.B. Caland et al. studied for the quantitative determination of sodium, potassium, calcium and magnesium inorganic cations in biodiesel samples [5]. Linlin Hu et al. determined the acetate, formate and propionate organic anions by ion chromatography [6]. Yi Zhang

et al. determined directly phosphate anion in raw *Jatropha curcas* oil by ion chromatography [7]. The content of phosphorus in biodiesel comes from the raw materials, such as seed oils and animal fats. The maximum concentration of phosphorus element allowed is $10\text{mg}\cdot\text{Kg}^{-1}$ according to the Brazilian norms, ASTM D6751 norms, DIN E 51606, ON C 1191, journal official, UNI10635 and SS 155436. However, the value according to the EN 14214 is $12\text{mg}\cdot\text{Kg}^{-1}$ and the CSN 65 6507 is $20\text{mg}\cdot\text{Kg}^{-1}$. The phosphorus compounds can inactivate the catalytic convertors of vehicles, increasing the ambient problem [8].

Like phosphorus, sulfur is also a typical poisonous catalyst and therefore can affect catalytic convertors [9]. Under China laws, the maximum sulfur concentration allowed is $10\text{mg}\cdot\text{Kg}^{-1}$. The regulated analytical methods is SH/T0689. Fluoride, chloride, bromide as the halogen elements have instability characteristics. Their presence can accelerate the corrosion of metals and can easily cause pitting [10-12]. Especially bromide, even at low concentration, can burn the surface, forming a rust corrosion. Bromide can also make sulfur dioxide oxidizing into sulfuric acid, and produce the liquid hydrobromic acid. It is fatal to the corrosion of the equipment. Therefore the application process must be paid attention to its prevention and control. In addition, the hydrogen fluoride gas biodiesel emitted is serious to our health. The maximum concentration of hydrogen fluoride allowable is 2

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mg·m⁻³[13] in the air of workplace. A certain amount of nitrate anion is also corrosive to pipes, and with the increase of nitrate, sulfate and phosphate anions concentrations, the degree of corrosion of pipes is more severe. Therefore, simultaneous quantitative analysis of inorganic anions in commercial waste-oil biodiesel using suppressed ion exchange chromatography is extremely important [14].

Ion chromatography has been applied to a variety of matrixes, including water [15-17], environment [18], food [3, 19-24] and medicine [25-29]. However, despite its versatility, this technique is rarely used for the analysis of biodiesel. Considering the variety of biodiesel matrixes, the pretreatment procedures enjoy separation funnels and cleaner IC(C18) which are enough for the elimination of the organic matter that interferes the analysis. The aim of the present work was the simultaneous quantitation of anions in waste-oil biodiesel using this procedure and technique.

EXPERIMENTAL

Instruments

A Metrohm 883 Basic IC plus is operated with the Magic Net Basic software. The instrument equipped with a dialysis system and a high pressure pump. A Na₂CO₃ (3.2mmol·L⁻¹) and NaHCO₃ (1.0 mmol·L⁻¹) aqueous solution was used as the eluent. The volume of the sample loop was 20 μL, and the intelligent separation column is a Metrosep A Supp 5(4×150mm) IC anion column. Inline filters protect the separation column securely against possible contamination from the eluent.

Reagents, solutions and samples

Reagents. Fluoride, chloride, bromide, nitrate, sulfate and phosphate anions standard solutions were purchased from J&K (Beijing, China). The aqueous solutions were prepared with deionized water, ultrapure Type 1(18.2MΩ·cm⁻¹ at 25°C). Ultra-pure sulphuric acid (99%) was purchased from Aladdin(Shanghai, China), and used to prepare a 1.0mmol·L⁻¹ sulphuric solution for the regeneration solution of the MSM. Sodium carbonate and sodium hydrogen carbonate were of analytical grade and also purchased from Aladdin (Shanghai, China).

Solutions. All standard solutions were shook prior and then were pipetted adequate volumes of the individual solutions to the volumetric flask(marked 100mL) and diluting them with ultra-pure water to reach a final volume: fluoride(0.5; 1.0; 2.0; 4.0;10.0mg·L⁻¹),chloride(0.5; 1.0; 2.0; 4.0;10.0mg·L⁻¹), bromide(0.5; 1.0; 2.0;

4.0;10.0mg·L⁻¹), nitrate(0.5; 1.0; 2.0; 4.0;10.0mg·L⁻¹), sulfate(0.5; 1.0; 2.0; 4.0;10.0mg·L⁻¹) and phosphate(0.5; 1.0; 2.0; 4.0;10.0mg·L⁻¹). All of the standard solutions were kept tightly capped and stored in polyethylene flasks under the ambient.

Samples. The biodiesel samples prepared from waste cooking oil (WCO) was furnished by industry, and a two-step catalyzed process was adopted to prepare biodiesel [30].

Analytical procedures. Separation funnel assisted liquid-liquid extraction

For the chromatographic determination of inorganic anions, a 100ml aliquot of 400ml waste-oil biodiesel and 30ml of ultra-pure water were introduced in a separation funnel. The separating funnel is set aside to allow for the complete separation of the phases. When two layers share a surface, the top are then opened to allow pressure equalization between the inside of the funnel and the atmosphere and the lower phase namely the aqueous phase is released into a 200ml volumetric flask by gravitation. When the aqueous phase has been removed, the stopcock is closed. The upper layer, i.e. the oily one was extracted again with the same extraction durations as previously described. Aqueous phase was again recovered and added to the first extract, up to the mark with ultra-pure water, and the recoveries of all samples are 100% in this extraction method. This experiment found that the concentrations of individual analytes are highest when the extraction times were 5. The results were shown in Figure 1 which was obtained from the Origin software.

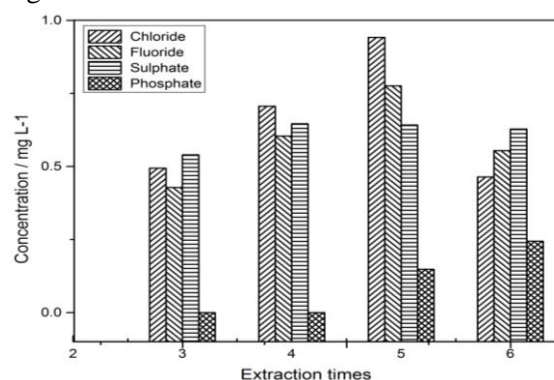


Fig. 1. The relation between extraction times and the concentration of individual analytes acquired by ion chromatography.

Assays for the spike-and-recovery

In order to verify the accuracy of the extraction process used, spike-and-recovery tests were performed by adding known concentrations of these six standard solutions to the biodiesel samples

prepared from the industry. And then by extractions and fixed the volume. Extractions were done as described above in section 2.3.1.

RESULTS AND DISCUSSION

Validation of the method

Important parameters for evaluating the determination methods are the linearity, the limits of detection, precision and accuracy.

Linearity

All standard solutions containing fluoride, chloride, bromide, nitrate, sulfate and phosphate anions were pipetted adequate volumes to the volumetric flask (marked 100mL) and diluting them with ultra-pure water to reach a final volume. The

experiment results were obtained in the Table 1, the calibration curves, $A = a + bQ$, were obtained by plotting the chromatographic peak area, the peak area is proportional to the amount of substance. The Y axis is the peak area A ($\mu\text{s}\cdot\text{cm}^{-1}\cdot\text{min}$) and the X axis is the concentrations, Q , of the analytes. The experimental correlation coefficients of the linear regression indicated a first order correlation in all analytes, Figure 2 which was exported from the IC software presented a chromatogram, the negative peak in the front of the chromatogram is the solvent peak and here is the water peak which will be contained in every chromatogram during this work.

Table 1. Linear equations of fluoride, chloride, bromide, nitrate, sulfate and phosphate anions. Analytic column: Metrosep A Supp 5(4×150mm), Eluent solution: Na_2CO_3 (3.2mmol·L⁻¹) and NaHCO_3 (1.0mmol·L⁻¹)

Anion	Concentration range (mg·L ⁻¹)					Analytical equation		r	RSD(%)
						A=a+bQ			
	a	b							
Fluoride	0.5	1.0	2.0	4.0	10.0	0.424145	0.138213	0.999987	0.062
Chloride	0.5	1.0	2.0	4.0	10.0	-0.409435	0.084848	0.999271	0.29
Bromide	0.5	1.0	2.0	4.0	10.0	-0.0610795	0.0202499	0.999805	0.036
Nitrate	0.5	1.0	2.0	4.0	10.0	-0.0468779	0.0228129	0.999792	0.042
Sulfate	0.5	1.0	2.0	4.0	10.0	-0.0256933	8.85E-03	0.99988	0.012
phosphate	0.5	1.0	2.0	4.0	10.0	-0.023412	0.0210993	0.999826	0.035

Table 2. The limits of detection (LOD) obtained for the chromatographic separation and determination of the studied anions in waste-oil biodiesel. Analytic column: Metrosep A Supp 5(4×150mm).Eluent solution: Na_2CO_3 (3.2mmol·L⁻¹) and NaHCO_3 (1.0 mmol·L⁻¹).

Anion	H _N (μS)	C ($\mu\text{g}\cdot\text{mL}^{-1}$)	H (μS)	V (μL)	C _{min} ($\mu\text{g}\cdot\text{mL}^{-1}$)
Fluoride	0.0025	0.5	1.731	20	0.0012
Chloride	0.0025	0.5	0.698	20	0.0029
Bromide	0.0025	0.5	0.173	20	0.0116
Nitrate	0.0025	0.5	0.224	20	0.0089
Sulfate	0.0025	0.5	0.075	20	0.0094
Phosphate	0.0025	0.5	0.212	20	0.0267

H_N-baseline noise peak-peak value, μS ; C-concentration of a standard solution, $\mu\text{g}\cdot\text{mL}^{-1}$;H-the chromatogram height of a standard solution, μS ; V-The volume of the sample loop, μL ;C_{min}-the minimum detection concentration, $\mu\text{g}\cdot\text{mL}^{-1}$

Table 3. RSD of the mean peak height values observed for the fluoride, chloride, bromide, nitrate, sulfate and phosphate anions.

Anion	The mean peak height value(μS)	RSD(%)
fluoride	28.044	0.062
chloride	16.713	0.290
bromide	4.008	0.036
nitrate	4.537	0.042
sulfate	1.750	0.012
phosphate	4.215	0.035

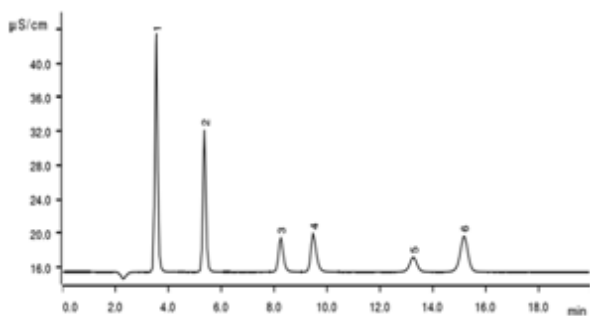


Fig.2. Chromatogram of the standard solutions. Peaks: (1) fluoride(9.992 mg·L⁻¹);(2) chloride(10.090 mg·L⁻¹); (3) bromide(10.046 mg·L⁻¹); (4) nitrate(10.047 mg·L⁻¹); (5) phosphate (10.035 mg·L⁻¹) and (6) sulfate (10.045 mg·L⁻¹).

The limits of detection

The limits of detection (LOD) is the minimum concentration of an analyte. According to the JJG 823-2014 Verification Regulation of Ion Chromatographs [31], LOD were calculated according to the following Formula 1 (The injection volume is 25µL).

$$C_{\min} = \frac{2H_N \times C \times V}{25H} \quad (1)$$

The limits of detection obtained from the proposed method in µg·mL⁻¹ were respectively: fluoride 0.0012µg·mL⁻¹; chloride 0.0029µg·mL⁻¹; bromide 0.0116µg·mL⁻¹; nitrate 0.0089µg·mL⁻¹; sulfate 0.0094 µg·mL⁻¹ and phosphate 0.0267µg·mL⁻¹. In all cases the observed LOD values were below 0.02 µg·mL⁻¹ that meets the performance indicators of IC Conductivity Detector. The obtained experimental results are shown in Table 2.

Precision. The precision was evaluated according to the repeatability and was expressed as relative

standard deviation (RSD). The chromatography parameter, the peak height values of the analyses were studied to evaluate the repeatability. A standard solution (10mg·L⁻¹) containing these studied anions was analyzed eight times by consecutive injections into the chromatograph. The mean values obtained for the peak height of the analyses and their RSD values were analyzed and shown in Table 3. It can be concluded that the method presents good repeatability because in all cases the observed RSD values were below 1%.

Accuracy

The accuracy of the proposed extraction method was evaluated through the spike-and-recovery tests. Waste-oil biodiesel samples were spiked with two different concentrations of standard solutions. All samples were filtered through cleaner IC-C18 before IEC analysis. Recoveries were calculated according to the Formula 2 obtained from analysis:

$$\text{Recovery} = \frac{\text{Found} - \text{Initial}}{\text{Added}} \times 100\% \quad (2)$$

The effect of frequency of liquid-liquid extractions was studied and the obtained results from the experiments were given in Table 4.

The biodiesel samples presented recoveries spanned from 78.4% to 110%(Table 4), indicating that the suggested extraction method was sufficiently efficient to remove the anions in the complex matrixes. Currently, in analytical procedures, recovery percentages in the range from 70 to 120% are accepted. However, depending on the complexity of matrix, this range can be extended from 50 to 120%[32].

Table 4. Recoveries of the fluoride, chloride, nitrate, sulfate anions in waste-oil biodiesel by ion chromatography.

Anion	Concentration (mg·L ⁻¹)			Recovery(%)
	Initial	Added	Found	
Fluoride	0.756	0.7	1.4077	93.1
		1.4	2.0944	95.6
Chloride	3.53	3.0	6.488	98.6
		6.0	9.188	94.3
Bromide	ND	0.1	0.089	89
		0.2	0.199	99.5
Nitrate	ND	0.2	0.22	110
		0.4	0.4068	101.7
Sulfate	0.782	0.8	1.5132	91.4
		1.6	2.2348	90.8
Phosphate	0.262	0.3	0.4972	78.4
		0.6	0.8038	90.3

ND=not detected

Analysis of the biodiesel samples

Aliquots of the biodiesel samples were analyzed by IEC after aqueous extraction according to the method described above. In all of the samples, the anions concluding fluoride, chloride, phosphate, sulfate were detected. The ion chromatographic results from this work were listed in Table 4. Figure 3 which was exported from the IC software presented the chromatogram for the waste-oil biodiesel samples purchased from the industry.

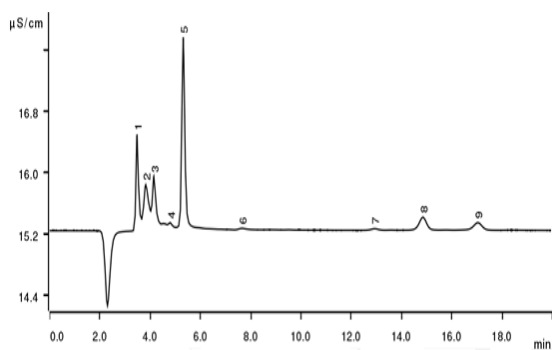


Fig. 3. Chromatogram of the aqueous extract of the biodiesel prepared from waste-oil biodiesel.

Peaks:

(1)fluoride($0.756\text{mg}\cdot\text{L}^{-1}$);(5)chloride($3.53\text{mg}\cdot\text{L}^{-1}$);(7)phosphate($0.262\text{mg}\cdot\text{L}^{-1}$);(8)sulfate($0.782\text{mg}\cdot\text{L}^{-1}$);(2,3,4,6,9):not spiked analyses

A blank experiment was done in order to verify the impact of deionized water used above on the experimental results. It found that no analyte is detected. It is also indicated that the deionized water has no effect on the study. Therefore, this work is successful and makes sense. Figure 4 which was exported from the IC software presented the chromatogram of the blank experiment.

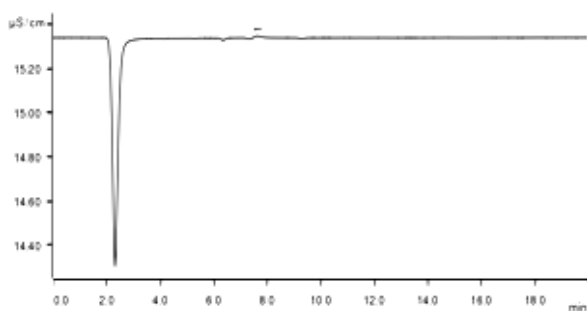


Fig.4. Chromatogram of deionized water used above in the extraction procedure. (1):not spiked analytes.

CONCLUSION

In this work, the liquid-liquid extraction procedure with water proposed was shown to be efficient. According to the results, Sulfate anion has the highest concentration in all of the samples from the industry, this may be responsible for using the

ferric sulfate in the first step of producing biodiesel. Chloride anion also presented a relatively high concentration in comparison to the other analytes acquired, it may result from the edible salt in waste-oil biodiesel. All of the analyzed samples presented low concentrations of fluoride and phosphate. Considering concentrated hydrohalic acid solutions produce visible white fumes, so this method is free from ultrasound heating for keeping from HF, HBr and HCl volatilizing, which may affect the experimental results greatly. The increasing use of biodiesel around the world implies a necessity to control the quality of this product. Therefore, the development of new and reliable analytical methods is necessary.

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