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Metal and metalloid determination in biodiesel and bioethanol

Raquel Sánchez,[a] Carlos Sánchez,[a] Charles-Philippe Lienemann,[b] José-Luis Todolí[a*]

[a] Department of Analytical Chemistry, Nutrition and Food Sciences, P.O. Box 99, 03080, Alicante, Spain

[b] IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP 3, F-69360 Solaize – France

Abstract

Biofuels quality control involves the determination of metal and metalloid content. These species play a very important role because they may modify the efficiency of the biofuel production as well as the stability of these products. Furthermore, some metals are toxic and generate environmental concerns whereas others are used as additives. Normally, products such as biodiesel and bioethanol are mixed with fossil conventional fuels (diesel and gasoline, respectively). Therefore, metals come from the raw product employed for biofuel production (seeds, sugars…) as well as from the production and stocking process or even from the added fuels. The determination of the final metal and metalloid concentration in biofuels is a challenging subject because of several reasons. On the one hand, their content is usually low (*i.e.*, from several μg L^{-1} to mg L^{-1}) and, hence, sensitive techniques should be used. Besides all this, calibration with organic complex matrices becomes more difficult and degrades the accuracy of the determination. Several approaches have been evaluated to carry out this kind of analysis going from spectrochemical to electroanalytical techniques. Within the first group, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Mass Spectrometry (ICP-MS) are often employed together with Atomic Absoption methods. The different procedures applied will be discussed in the present review emphasizing the most widely employed ones. On this subject, fundamental as well as applied studies related with the biofuels analysis through ICP-OES and ICP-MS will be shown to illustrate the current difficulties associated to these determinations. Comments regarding to the possible solutions proposed to overcome the drawbacks encountered will be made.

5. Conclusions
6. Literature

1. General Introduction

Nowadays, the interest in the development of energy sources alternative to fossil fuels has increased significantly. The most widely used biofuels are bioethanol and biodiesel and their increasing demand involves the development of new methods to assure the quality of the final products. In this sense, the determination of metals and metalloids plays a fundamental role. Within this category one can find alkaline and alkaline earth elements (Na, K, Ca, Mg), heavy metals (Cd, Zn, Cr, Fe, Mn and so one), metalloids (As, B) and non metals such as S or P. These elements are present at variable concentrations depending on factors such as the raw materials, production process and the post-production pollution, among others. Because the presence of these elements may affect the quality of the biofuel, official specifications have appeared. For example, ASTM D6751 in the USA and EN 14214 in Europe are specifications related with biodiesel quality requirements. Table 1 shows that both standards differ in some points. In the case of bioethanol, some specifications refer to the so called ethanol fuel that corresponds to an ethanol-gasoline blend. In general terms, it can be stated that there is no information regarding the maximum allowable level of heavy metals in biodiesel and bioethanol.

Table 1. Standard Specifications and maximum allowable levels of metals and metalloids.

Biofuel	Element(s)	Content	Standard*	Year
Biodiesel	Na + K (Group I metals)	5 mg Kg^{-1}	ASTM D6751/ EN 14214$^{\#}$	2012/2014

	Ca + Mg (Group II metals)	5 mg Kg^{-1}	ASTM D6751/ EN 14214[#]	2012/2014
	S	Two grades: S15 (15 mg Kg^{-1}) S500 (0.05%)	ASTM D6751/ EN 14214[#]	2012/2014
	P	0.001% (w/w)	ASTM D6751/ EN 14214[#]	2012/2014
Ethanol fuel	S	30 mg Kg^{-1}	ASTM D4806	2014
Bioethanol	Cu	0.1 mg Kg^{-1}	EN 15488/ASTM D1688/JIS K0101	2007/2012/1998
	P	0.5 mg L^{-1}	EN 15487/ASTM D3231	2007/2013
	S	10 mg Kg^{-1}	EN 15487/ ASTM D3231	2007/2013

[#] Applies only to Fatty Acid Methyl Esters (FAME)

* References for test methods are given in the case of bioethanol.

The quantification of metals and metalloids in bioethanol and biodiesel has several difficulties associated: *(i)* some of them are present at very low concentrations (μg L^{-1}); *(ii)* there are limited certified reference materials, see Table 2; *(iii)* commercially available bioethanol, for instance, exists in a large variety of matrices with different water content; *(iv)* several sources of raw materials can be employed affecting the characteristics of the final product; and, *(v)* bioethanol and biodiesel contain around 300 different organic compounds depending on its origin and treatment[1,2] .

Table 2. Biodiesel and bioethanol based products CRMs

Matrix	Element	Concentration	Source	Web
Biodiesel	Na, K	2.5 - 50 µg/g	LGC	www.lgcstandards.com
Biodiesel B100	Ca,K,Mg,Na,P	2.5 - 50 µg/g	LGC	www.lgcstandards.com
Biodiesel B100	S	5 – 500 µg/g	LGC	www.lgcstandards.com
Biodiesel B5	S	5 – 500 µg/g	LGC	www.lgcstandards.com
Biodiesel B20	S	5 – 500 µg/g	LGC	www.lgcstandards.com
Biodiesel	Ca, Mg	2.5 - 50 µg/g	LGC	www.lgcstandards.com
B100 Biodiesel (Soy-Based) SRM -2772	Ca Cu Fe Mg P K Na	0.5 mg/kg <0.2 mg/kg <0.2 mg/kg <0.2 mg/kg <0.4 mg/kg <0.1 mg/kg 0.07 mg/kg	National Institute of Standards & Technology	http://www.nist.gov/
B100	Ca	0.1 mg/kg	National	http://www.nist.gov/

Biodiesel (Animal-Based) SRM -2773	Cu Fe Mg P K Na	<0.2 mg/kg <0.2 mg/kg 0.05 mg/kg <0.4 mg/kg <0.1 mg/kg 0.9 mg/kg	Institute of Standards & Technology	
Reformulated gasoline	S	13.6 µg/g	LGC	www.lgcstandards.com
Reformulated gasoline	S	13.8 mg/kg	National Institute of Standards & Technology	http://www.nist.gov/

*Reformulated gasoline has a 10% of ethanol content (fuel ethanol E10).

For all these reasons, it is obvious that sensitive techniques are required to carry out the determination of metals and metalloids in this type of samples. In addition, it is necessary to develop analytical methods able to compensate for matrix effects due to large variety of matrices found in bioethanol and biodiesel samples. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Mass Spectrometry (ICP-MS) appear as the most appropriate techniques to perform elemental determinations in biofuels, although alternative techniques have also been applied for this purpose.

The fundamentals, applications and latter developments of biodiesel and bioethanol analysis through ICP techniques are revisited in the present work. The use of alternative analytical techniques for this purpose is also mentioned.

2. Fundamental studies

In order to understand the phenomena occurring when organic samples such as biodiesel and bioethanol are introduced into Inductively Coupled Plasma, fundamental studies are required. This kind of samples may interfere on each step of the sample analysis from the aerosol production to the signal recording. Additionally, due to the high viscosity of biodiesel, for instance, a pretreatment step of the sample is usually required. The dilution with a proper solvent is the most extended procedure ethanol, kerosene and xylene being usually employed for this purpose.[3–5] Bioethanol, in turn, may contain variable proportions of water, propanol, butanol and other low molecular weight alcohols[1]. Therefore, the physico-chemical properties of the sample will change thus causing an intensification of the matrix effects.

2.1. Aerosol generation

When a pneumatic nebulizer is used to generate the aerosol, the solution physical properties affect the characteristics of the produced mist. For this kind of nebulization devices, the most important properties are the surface tension and the viscosity. Organic samples, such as those included in the terms bioethanol and biodiesel, have a quite wide range of viscosities and surface tension values. Table 3~~Table 2~~ summarizes the density, viscosity and surface tension for representative FAME and biodiesel samples. Moreover, two synthetic solutions usually prepared to simulate the blanks also included. In this case, the portion of biodiesel was replaced by an Element Stock Oil (75 Viscosity, Conostan, Ponca City, Oklahoma, USA). As it may be observed, viscosity is different according to the particular solution considered.

Table 3. Density, viscosity and surface tension at 20ºC for the different samples.

Sample	**Viscosity (cP)**	**Density (g cm^{-3})**	**Surface tension (mN m^{-1})**
FAME – Xylene 1:1	2.5	0.83	n.a.
Stock oil – Xylene 1:1	1.5	0.84	30.0
FAME –Kerosene 1:1	3.2	0.84	n.a.
Stock oil – Kerosene 1:1	1.9	0.84	29.5
Xylene	0.6	0.85	27.5
Biodiesel	5.1	0.84	31.4
Biodiesel : Xylene 1:10	0.7	0.85	28.8
Ethanol	1.14	0.79	22.3
Water	1.00	1.00	72.8
Bioethanol	n.a.	0.82	23.3

In order to evaluate the influence of solution physical properties on the nebulizer performance, the aerosols produced in a first instance (*i.e.*, primary aerosols) can be measured. Farino and Browner[6] studied the effect of the sample surface tension on the aerosol properties. As this physical property decreases, the energy required to generate a droplet from the solution bulk goes down. In addition, in solvents with low surface tension, the waves generated on the liquid surface have a short wavelength and the gas penetrates easily into the liquid bulk. As a result, the liquid and gas interaction becomes highly efficient, thus favouring aerosols with low droplet diameters. For example, when a pneumatic concentric nebulizer is operated under typical conditions (*i.e.*, 1 mL min^{-1} liquid flow rate and 0.7 L min^{-1} nebulizer gas flow rate) the median of the aerosol volume drop size distribution (D_{50}) for primary aerosols are 17 and 11 μm for water and ethanol, respectively. It is worth mentioning that surface tension for ethanol (21.4 dyn cm^{-1}) is approximately three times lower than for water, whereas both solvents have similar viscosity values.[7]

Regarding viscosity, as Sharp studied, the instabilities generated on the liquid surface during the nebulization event are attenuated for liquids with high viscosity values of ,[8] thus promoting the generation of coarse aerosols. As Table 3~~Table 1~~ reveals, final viscosity depends on the solvent employed to dilute the sample, thus affecting the primary aerosol characteristics. Thus, for instance, for a pneumatic concentric nebulizer, when xylene is used to dilute the samples, all the primary aerosol liquid volume is contained in droplets with diameters below 13 μm, whereas this maximum diameter increases up to 17 μm when the employed solvent is kerosene.

In the case of biodiesel, the D_{50} takes values of 11, 63 and 23 μm for xylene, biodiesel and 1:10 diluted biodiesel, respectively. As expected, compounds with low viscosities promote the production of fine aerosols.[8,9] It is also worth to notice the poor nebulization yield observed for a pure biodiesel sample. Due to the high D_{50} value, the sensitivity finally obtained will be extremely low. The proposed solution to generate finer aerosols is, thus, to dilute the sample with an appropriate solvent.

In the case of bioethanol, the final sample composition may vary as a function of several factors among them the water content or the additives present. This fact is illustrated in Figure 1~~Figure 1~~ in which the Sauter mean diameter, $D_{3,2}$, significantly changes as a function of the sample considered.

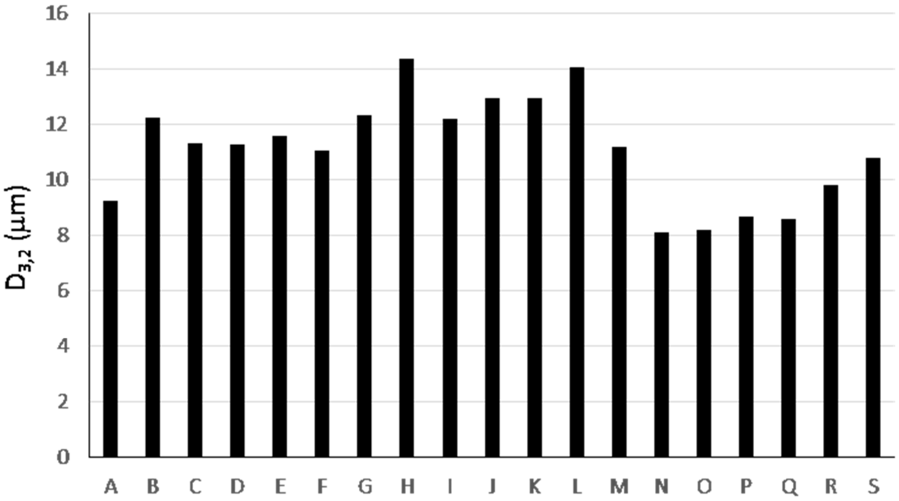

Figure 1. Sauter mean diameter ($D_{3,2}$) for primary aerosols generated by a conventional pneumatic concentric nebulizer working with 19 different bioethanol samples (A-S).

2.2. Aerosol transport

Once the aerosol is generated, several phenomena take place inside the spray chamber that lead to a modification in its characteristics. These are the so-called aerosol transport phenomena and they are responsible for analyte losses inside the spray chamber. The most influencing events are: *(i)* solvent evaporation; *(ii)* droplet coalescence, and; *(iii)* droplet inertial impacts. The major changes in the primary aerosol characteristics are caused by the nebulizer gas flow rate and the design of the spray chamber.[10] However, the primary aerosol characteristics together with sample physical properties, mainly density and volatility, affect the extent of all these processes.

In the case of organic saamples, the solvent volatility is the most relevant property precluding the mass of solution delivered to the plasma. The solvent evaporation takes place mostly just after the aerosol generation until the gas becomes saturated in solvent. The high solvent volatility together with the fineness of the organic aerosols contribute to an enhancement in the mass of analyte and solvent delivered to the plasma.[11,12] Under these circumstances, nebulization conditions (liquid and gas flow rates) have a more determining effect for organic solvents than for aqueous solutions. Thus, for volatile solvents, the solvent transport efficiency may reach values close to 100%. Therefore, the selection of the appropriate experimental conditions is a more challenging issue for the formers.[13]

The fineness of the aerosol leaving the spray chamber (tertiary aerosol) and the mass of solvent and analyte transported to the plasma are indicators of the quality of the primary aerosol transport. In fact, the drop size distribution of the tertiary aerosol is proposed by several authors as the property that plays a major role in terms of plasma thermal state because it determines the amount of energy required to vaporize the matrix.[14] On this subject, finer aerosols are found when working with 50% (v/v) ethanol – water mixtures than for water alone. These results are independent of the spray chamber considered.[15] A stirred tank methodology has been used to thoroughly study the effect on increasing the ethanol concentration on the characteristics of the aerosols leaving the spray chamber.[16] The results proved that the median of the tertiary aerosol volume drop size distribution decreased significantly as the concentration of this alcohol went up to 5 %. Then the decrease in this statistical parameter with the ethanol content became less pronounced. The intensification of the solvent evaporation inside the spray chamber and the fineness of the generated aerosols as the ethanol proportion grows appear to be the dominating phenomena.

The evolution of drop diameter versus time as a result of the solvent evaporation is a function of the so-called evaporation factor[12] which is defined as the volume of solvent evaporated per unit of time. This magnitude can be calculated according to:

$$E = 48 D_v \sigma P_s M^2 (\partial R T)^{-2} \qquad \text{Equation 1}$$

where D_v is the vapor diffusion coefficient, σ the solvent surface tension, P_s the saturated vapor pressure, M the molecular weight ∂ the solvent density , R the gas constant and T the temperature.

As Boorn *et al*[17] reported, the solvent evaporation factor for ethanol is about three times higher than evaporation factor for water ($E_{ethanol} = 45.6\ \mu m^3/s$ vs $E_{water} = 13.1\ \mu m^3/s$).

As a result of the finer aerosols and the higher evaporation factor, the total mass of solvent transport rate leaving the chamber for a pneumatic nebulizer adapted to a double pass spray chamber was 6 times higher for ethanol as compared to water. Note that the relative volatility values were 0.1 and 0.7 for water and ethanol, respectively.[7] As the solvent evaporation becomes more significant and finer aerosols are generated for ethanol than for water, droplets decrease their diameters and they have more chance to be transported through the spray chamber. The net result is an increase in the analyte transport rate for the former. In the particular case of ethanol samples, this parameter was about five times higher than for water.

2.3. Plasma effects.

When carrying out the analysis of bioethanol or biodiesel samples, plasma effects should be carefully considered. These effects are related with the plasma energy consumed for the solvent vaporization and dissociation. Obviously, the operating nebulization conditions (*i.e.*, the liquid flow rate and nebulizer gas flow rate) play a fundamental role, because they dictate the aerosol mass reaching the plasma. For instance, it is sometimes advisable to lower both variables so as to reduce the solvent plasma load, simultaneously increasing the residence time of the analyte in the plasma.[18] Nevertheless, if these variables (especially the nebulizer gas flow rate) are excessively decreased, the analyte mass transported towards the plasma and, hence, the sensitivity may be too low. Plasma degradation caused by the presence of bioethanol or biodiesel becomes less pronounced at high R.F. power values. Under these conditions, sensitivities may be higher for organic samples than for aqueous matrices. In contrast, if plasma effects are not taken into consideration, organic solvents may cause a decrease in the sensitivity.[19]

Several studies have been conducted in order to try to understand the effects caused by the presence of an organic matrix on the plasma performance. When an organic sample (*e.g.* ethanol, biodiesel) is introduced into the ICP, specific effects take place such as: *(i)* molecular emission of solvent pyrolysis products; *(ii)* modifications in the plasma geometry; *(iii)* generation of vortex in the plasma; *(iv)* changes in electron number density, hydrogen density and excitation temperature; and, *(v)* formation of carbon or soot deposits somewhere in the spectrometer.

Molecular emission of solvent pyrolysis products

The incomplete combustion of organic solvents yields some molecular species, not observed in the case of aqueous solutions, that are excited in the plasma. The molecular emission bands can spectrally interfere on the analytical emission. In ICP-OES, Boorn *et al*.[17] observed a green C_2 emission zone around the outside of the plasma. Additionally, cyanide radical (410-430 nm)[20] and diatomic carbon (450-520 nm) emissions are produced in the boundary regions of the discharge whereas atomic carbon emission is observed in the plasma region.[21] These emissions contribute to increase the background level. The intensity of these emissions depends on the plasma observation height.[10,14,17,22] Thus, carbon atomic emission decreased with observation height whereas cyanide emission showed an opposite behavior.

Modifications in the plasma geometry

Weir and Blades[20] verified that in presence of organic solvents the plasma moved downstream and its central channel dilated. They also observed that these effects became more significant as the solvent load increased. Therefore, ethanol loading could drastically modify the energy available at the plasma central channel.

The introduction of an organic solvent may increase the thermal conductivity hence accelerating the heat conduction away from the plasma. As a result, the peripheral zones of the plasma cool rapidly thus causing a reduction in the plasma volume. This is the so-called plasma thermal pinchthat has been observed when introducing solvents such as methanol and can be extrapolated to ethanol[20] and ethanol-water solutions.[14,23]

Vortex generation in the plasma

One of the most important plasma fluctuations is a result of vortex shedding beyond the exit of the torch. Weir and Blades[24] proved that vortex are present in ICP and this phenomenon causes modulation of emission. They observed that the vortex shedding frequency depended on the solvent and the solvent plasma load.[20,24]

Changes in electron number density, hydrogen density and excitation temperature

Studies dealing with plasma effects reveal that the presence of an organic solvent causes a decrease in excitation temperature[25,19,17] as well as in the electron number density.[26] However, it was found that n_e increased when ethanol concentration went from 0% to 25%. It was also reported that when pure water reached the plasma n_e was maximum at 5 mm from the center of the torch but for a 25% ethanol solution this radial maximum was located at the center of the torch.[10] In another study, the same authors indicated that the electron number density in the plasma central channel increased almost three times for ethanol, while at z=5 mm alc n_e was two times higher than for pure water.[22]

Of course, hydrogen emission and electron density depended on the operating conditions. As it has been reported, the effect of ethanol concentration on H emission intensity is more pronounced at low than at high RF power. At 1.02 kW the emission signal of hydrogen (434.05 nm) for 10% of ethanol was around 3 times higher than that obtained for water while at 1.36 kW this enhancement factor was only 2 times.[23]

Besides electron number density, plasma excitation temperature also changes when an organic solvent is delivered to the excitation cell. Several authors reported decreases in this parameter as compared to aqueous solutions.[17,19,22,23,26–29] However, a maximum pattern in the excitation temperature was reported as the ethanol content went up.[23,30]

A change in the hydrogen content can be claimed in order to try to explain the eventual increases in plasma fundamental parameters found when introducing ethanol. The effect of adding molecular hydrogen to the plasma has been previously described and its beneficial role on both n_e and excitation temperature has been demonstrated.[23,26,31–3435]The increase in hydrogen generation and, hence, the rise in the plasma thermal conductivity, in presence of ethanol with respect to water are based on the fact that the energy requirements to induce its dissociation are very low in comparison with those for water.

A parameter widely studied to monitor the plasma thermal state and its robustness is the magnesium ionic to atomic net emission intensity ratio (MgII/MgI). According to previous studies it has been indicated that this ratio increased with ethanol concentration up to 25%.[14] This trend was confirmed by the experiments done with a stirred tank setup. For a less robust plasma, it was found that the MgII/MgI ratio peaked at about 8% ethanol and then decreased.[16] Possible explanations could be based on the increased plasma thermal conductivity and/or thermal pinch. Once the ethanol plasma load becomes too high, a degradation in its excitation conditions is produced.

Formation of carbon or soot deposits somewhere in the spectrometer

Finally, the formation of carbon deposits in some parts of the spectrometer, such as injector or the torch walls may degrade the plasma stability.[4,36] Solvent evaporation factor can be connected with the limiting aspiration rate defined as that the maximum liquid flow allowing a stable plasma operation, with no appreciable carbon deposition on the inner torch surfaces.[17] Normally, the tolerance to solvents decreases when evaporation factor increases. Although ethanol shows moderate evaporation rates it causes a quick quenching in the plasma due to other effects related with the emission of solvent pyrolysis products. In order to avoid these problems, oxygen can be added to the carrier argon stream. This gas prevents the carbon (soot) deposition in the system.[37,38] However, if too much oxygen is added in ICP–MS, the cones can deteriorate and the polyatomic interferences can become more severe.

2.4. Spectral interferences

Spectral interferences caused by organic samples in ICP-OES are due to the solvent pyrolysis products. In presence of an organic solvent, the most abundant species in plasma are C_2, CN, and C. Furthermore, depending on the solvent nature, other molecules may be present such as CS, CH, NO and CO. Figure 2~~Figure 3~~ shows the evolution of the background emission spectrum versus the plasma observation height. When an alcohol is introduced into the plasma, spectral interferences are strongest at its base. Note that the plasma operating conditions can alter the distribution of the pyrolysis products.[39] Moreover, it is very important to take into account the physical form in which the solvent reaches the plasma because a large fraction of it is in vapor form.[19] Pan *et al.*[19] demonstrated that the main impact of desolvation with organic solvents is to reduce the C_2 species population in the plasma, which in turn strongly influences plasma temperatures.

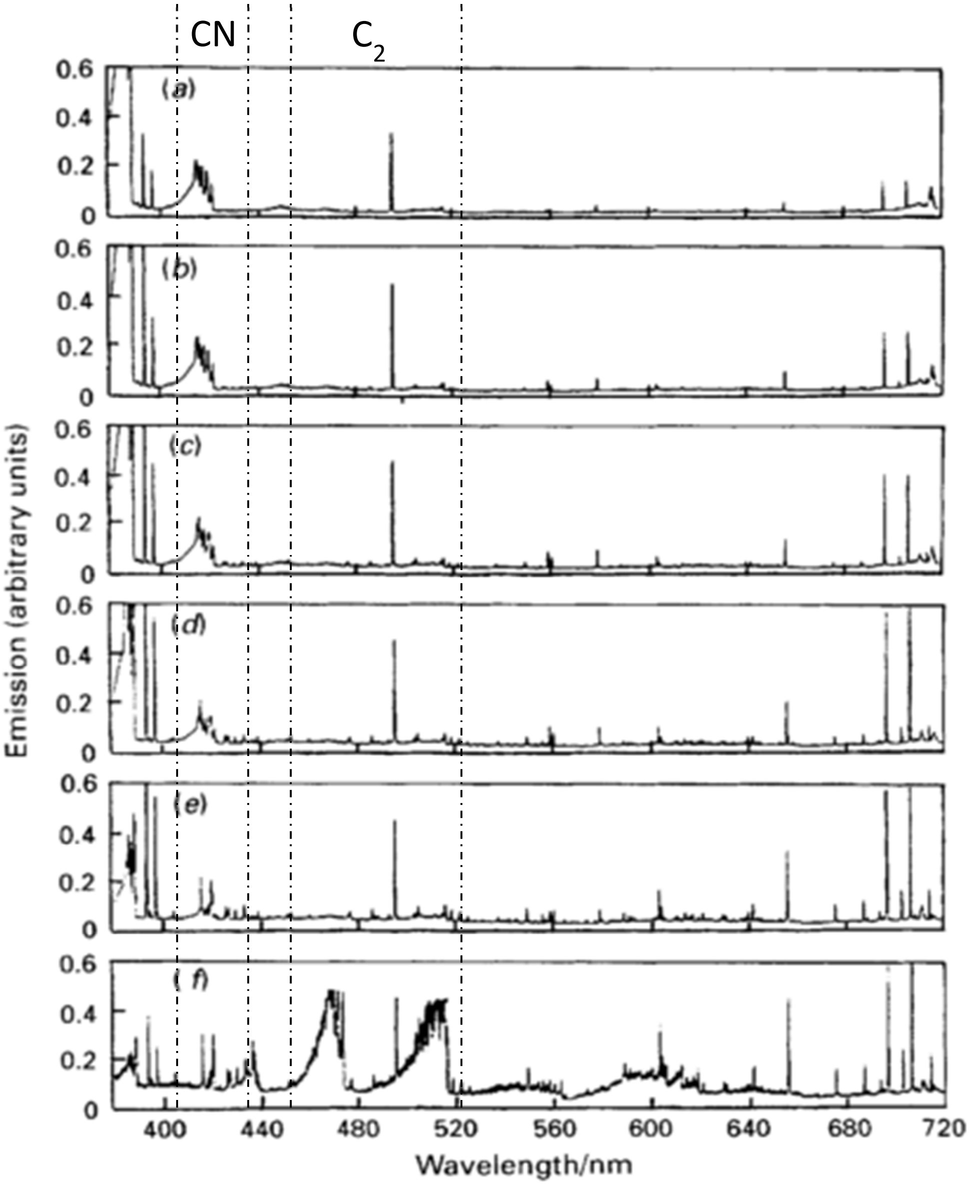

Figure 2~~3~~. Spectral survey of the visible emission from de ICP loaded with methanol for several observations heights: (a) 21 mm; (b) 18 mm; (c) 15 mm; (d) 12 mm; (e) 9 mm; (f) 6 mm. Cyanide radical (410-430 nm) and diatomic carbon (450-520 nm) Taken from ref. [20]

Alcohols also induce ICP-MS spectral interferences.[40–42] They can be explained in terms of: *(i)* charge transfer reactions from C species to the analyte ions;[43] *(ii)* enhancement of the aerosol transport efficiency through the sample introduction system;[44] and *(iii)* shifts in the plasma zone of maximum ion density.[45,46] The presence of ethanol[47] can lead to increases in the sensitivity for some isotopes because of polyatomic interferences. Also, for this technique, the interferences could be due to the formation of pyrolysis products.[48] In order to avoid these phenomena, collision and reaction cells can be employed. Woods *et.al.*[49] applied an ICP–MS fitted with an octopole reaction system (ORS) to the direct determination of the inorganic content of several biodiesel samples. Intense plasma-based species such as $^{14}N_2$ on ^{28}Si, $^{38}Ar^{1}H$ on ^{39}K and ^{40}Ar on ^{40}Ca were removed by reaction mode; in this case with H_2 cell gas. Sulfur, in turn, was measured removing the O_2 interference by reaction with Xe cell gas.

3. Biodiesel

Nowadays, there is an increasing demand for biodiesel production. In fact, the European Directive RED 2009/28/EC[50] promotes the use of substitute fuels coming from renewable, non edible origin. Among biodiesel, Fatty Acid Methyl Ester (FAME) is available as directly blended with diesel from fossil origin. In the last decade, the number of papers focused on biodiesel production has increased from 31, in 2003, to 1296 in 2013.

Generally speaking, biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids produced mainly by transesterification.[51] However, there are four primary ways to produce biodiesel: direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification .[52–57] For all these processes the resulting product shows a high combustion efficiency. In the case of pyrolysis, the obtained fuel is chemically similar to petroleum products. However, the main drawback of pyrolisis is the high amount of energy consumed in the cracking step. Meanwhile, in the case of the transesterification process, the main disadvantage is the formation of reaction by-products, such as glycerol and wastewater.

Alternative process have been developed, such as hydrogenation of fat towards kerosene /diesel, as well as FT synthesis. The most employed process is currently based on transesterfication.

3.1. Synthesis and presence of metals. Importance of their determination.

Most of the metals present in biofuel come from the raw material (*e.g.*, seeds) or are introduced during the processing or storage of the final product. Several inorganic contaminants may occur in the raw materials, mainly due to the absorption of some minerals from the soil where the plant was grown, other sources such as pesticides and fertilizers could be considered. Seeds, commonly employed for biodiesel production, with different origin were analyzed: castor bean, cotton seed, curcas bean, fodder turnip, sunflower, soybean and tung. After digestion of the seed, element concentrations were determined by ICP OES (Ca, K, Mg, Na and P) and by ICP-MS, using external calibration with aqueous standard solutions.[58] As it was expected the elements, whose concentration limit is regulated by international organizations [59,60] presented the highest concentration in the seeds. Regarding minor elements, Al, Fe, Mn and Zn concentration was strongly related to the the soil characteristics. The concentration of Al in the tung sample, about 200 μg g^{-1}, was at least 4 times higher than in the other seed samples. The maximum Fe concentration was found in the fodder turnip, about 130 μg g^{-1}. Zinc was more concentrated in the sunflower and in the castor bean samples, around 45 μg g^{-1}. The concentrations of Mn varied from about 7 μg g^{-1} in tung seeds to about 27 μg g^{-1} for curcas bean.[58] Paredes *et al.* has recently proposed the use of normalized ratios of mass fractions found for B, Fe, Cu, Zn, P and S as markers of the biological origin of raw materials of 1st generation biodiesels .[61] However, a clear relation between metal fingerprint and sample origin has not been established. Pillay *et al.*[62] demonstrated that sharp differences could exist due to the nature of the feedstock ensuing from differences in cultivation techniques, soil conditions and plant parts used for obtaining the biofuel.

Generally speaking, transesterification compromises the reaction between fats or oils, triglycerides and an alcohol, usually methanol or ethanol, in the presence of a catalyst to produce glycerine and methyl esters or biodiesel.[63] When methanol is employed the biodiesel is called FAME (fatty acid methyl esters), whereas for ethanol it is called FAEE (fatty acid ethyl ester). The catalysts employed could be classified mainly in four groups: *(i)* basic homogeneous; *(ii)* acid homogeneous; *(iii)* heterogeneous; and *(iv)* lipases. Basic catalyst are the most widely employed as they provide better reaction efficiencies. Among the basic catalysts sodium and potassium hydroxides, carbonates and sodium and potassium alkoxides, such as methoxide, epoxide, and nitrous dioxide are included. Sodium and potassium hydroxides are the most common basic catalysts in the industry.[64,65] However, in order to be able to use these catalysts, the raw material to obtain biodiesel, must be purified so as to remove free acids. This is because the basic catalyst neutralizes free fatty acids, which may cause the formation of soaps thus promoting the formation of stable emulsions. These emulsions do not allow separation of biodiesel and glycerine affecting the purification of esters.[66] Moreover, the separation of the catalysts from the reaction products in the purification steps is technically difficult precluding the quality of the final product.[67,4] The use of a suitable heterogeneous catalyst has been suggested by several research groups. The main advantage incorporated by heterogeneous catalysts is that they can be separated from the reaction products by filtration.[63,68–89]

In addition, it is important to note that the commercial biodiesel is a blend of the pure biodiesel (e.g. FAME, FAEE) and diesel. The European Union legislation established the maximum blend ratio in B7.5 (7.5% biodiesel, 92.5% diesel) for technical reasons.[90] Whereas, in certain non-european countries a percentage blend is mandatory. In Brazil, which has the world's most developed biofuels industry, a 25% blend is mandatory. On the other side, blends of 20% biodiesel and lower can be used in diesel equipment with no, or only minor modifications

For "pure biodiesel", metal content determination is important to ensure the quality of the final product. Some metals, especially sodium and potassium, could be incorporated to the final product during the transesterification reaction. Sodium and potassium compounds promote the formation of insoluble and abrasive solids contributing to the degradation of the engine parts or to the deposit formation in the vehicles filters.[91–93] Moreover, "pure biodiesel" may contain additional elements. For example some elements such as Cu, Cd, Ni, etc. could be absorbed from the soil by the the plant itself. In addition, the fingerprint in terms of metal in the "industrial biodiesel" gives an indication of the environmental risk. Moreover, some metallic species are incorporated to the product as additives: anti-knock agents, anti-oxidants, burn improver, metal deactivators, anti-rust agents, anti-icing agents, upper-cylinder lubricants, and detergents. In some instances, elements are incorporated into the product during transportation and/or production or storage.[92,94–96]

Finally, the presence of some metals can affect the stability of the biodiesel.[97–99] Sarin *et al.*[100] studied the influence of metal contaminants on oxidation stability of Jatropha biodiesel. The induction period of the biodiesel decreased drastically with small concentrations (mg kg^{-1}) of metal contaminants. The biodiesel exhibited oxidation stability of 3.95 h in Rancimat test, according to the EN 14112.[101] The biodiesel standard EN14214[59] required the oxidation stability determination at 110°C with a minimum induction time of 6 h by the Rancimat method[101] whereas the ASTM standard D-6751[60] recently introduced a limit of 3 h. The stability of biodiesel is critical to ensure fuel quality at all points along the distribution chain. Among the metals investigated, copper appears to have the strongest detrimental effect. Additional elements such as Co, Cu, Fe, Mn, and Ni can promote oxidative degradation, whereas some elements such as Pb, and Zn can also catalyze the biodiesel oxidation.[102,103]

3.2. Analysis by ICP techniques

Because the metal concentration in biodiesel is usually low; the selection of the determination technique should be strongly related to the target metal and to its concentration.[104] The main techniques employed are flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). [4,49,91–94,103–110]

3.2.1. Conventional sample introduction systems and electrothermal vaporization

The first work devoted to the use of ICP-OES for the determination of metals in biodiesel was conducted by Edlund *et al.*[4] This work was focused on the development of a method for the determination of six analytes: Ca, K, Mg, Na, Cl and P. In this case, an argon-oxygen mixed-gas was used to reduce the extent of spectral interferences related to carbon and carbon compounds. In fact, for Na and K, an increase in the signal to background ratios was observed thus lowering the limits of detection. LODs obtained with the argon-oxygen mixed gas were 7.1, 1.6 and 1.4 mg kg^{-1} for K 766.490, Na 588.995 and Na 589.592 nm, respectively; whereas operating in the conventional mode, the respective LODs were 220, 59 and 74 mg kg^{-1}. However, it was found that the LODs for Ca, Mg, P and Cl were not improved upon the addition of oxygen to the plasma. The determination of chlorine at low mg kg^{-1} levels was possible using the intense spectral lines at 134.724 or 135.166 nm.

Sample preparation

Dilution has been widely recommended as sample treatment method for the analysis of biodiesel. The selection of the solvent could influence the quality of the analytical results. Xylene and kerosene have been widely used to perform routine analysis of this kind of samples.[111–118] In the case of phosphorous determination by ICP-OES Sánchez *et al.*[119] employed two sample introduction systems: *(i)* a concentric micronebulizer fitted to a glass cyclonic spray chamber; and, *(ii)* the same nebulizer coupled to a glass single pass spray chamber (Torch Integrated Sample Introduction System, TISIS)[119–121].For the conventional cyclonic spray chamber, the signal enhancement factor observed for xylene with respect to kerosene ranged from 2.9 to 3.9. Similar trends were found for the TISIS although the influence of the solvent was less marked than that observed for the cyclonic spray chamber.

Ethanol was proposed as an alternative solvent by dos Santos *et al.*[3] for simultaneous determination of Ca, P, Mg, K and Na in biodiesel by ICP-OES. Dilution with ethanol enabled the use of aqueous standards, leading to accurate and precise results. An oxygen flow was used to decrease the background and non-spectral interferences were compensated for by employing yttrium as internal standard. The maximum allowed concentration [59,60] was higher than the limits of detection obtained with this procedure. The obtained LODs, considering 2.5 g of sample in a final volume of 25 mL, were: 0.03, 0.5, 0.005, 0.3 and 0.1 µg g^{-1}, for Ca, P, Mg, K and Na, respectively. Moreover, the validity of the method was evaluated throughout the analysis of four biodiesel samples produced from different raw materials. The samples were spiked with 5 µg $g^{-1}$of the analytes. Calibration was carried out with standard solutions containing an ethanol-water mixture as solvent. All recoveries were in the 82 to 114% range for all analytes, demonstrating the accuracy of the proposed procedure. Moreover, Chaves *et al.*[5] evaluated alternative solvents, as ethanol and 1-propanol, for the determination of Ca, Cu, Fe, K, Mg, Na, P, S and Zn in biodiesel and vegetable oils by ICP-OES. Calibration was carried out against inorganic standards diluted in ethanol or 1-propanol, while yttrium was used as an internal standard, correcting for non-spectral interference and sensitivity drift. Recovery tests yielded figures included within the 87 to 116% range. The measured precision expressed as relative standard deviation (n=3) was lower than 5% and limits of detection were at the low µg g^{-1} level.

While dilution of samples is one of the most widespread approaches, other alternatives have been explored (*e.g.*, emulsification) so as to reduce the mass of organic solvent introduced into the plasma.[122] The emulsification involves the addition of an aqueous phase containing an acid and/or surfactant in an appropriate proportion.[123] De Souza *et al.*[124] developed a simple and rapid method for the simultaneous determination of seven trace elements in biodiesel by axial and radial viewed ICP OES. The sample was emulsified with Triton X-100 and water, yttrium being employed as internal standard. One of the advantages of the emulsification was that aqueous standards could be used. Good recoveries, in the range of 90 to 109%, were achieved for all the studied analytes. Moreover, the LODs obtained in the axial mode went from 0.007 to 0.660 μg g^{-1}. Young *et al.*[125] developed a method for the determination of sulphur in biodiesel samples based on the sample micro-emulsification. Microemulsions were prepared using 0.5 mL of 20% v/v HNO_3, 0.5 mL of Triton X-100, 2–3 mL of biodiesel sample, and diluted with n-propanol to a final volume of 10 mL. The novelty of the method was the summation of the emission intensities of multiple sulphur lines to increase accuracy and sensitivity. The recoveries obtained ranged from 72 to 119%. Recently, the same emulsifier was used by Lisboa *et al.*[126] and, as in the previous work, external calibration with aqueous standard solutions was applied. LOD were in the sub-mg kg^{-1} range and recoveries went from 91 to 107%.

Moreover, the sample digestion was explored as alternative sample preparation method by Korn *et al.*[127] Two digestion procedures were evaluated for the determination of Ca, P, Mg, K and Na in biodiesel by ICP OES: *(i)* an open system with conventional heating using concentrated nitric and sulfuric acids and the addition of hydrogen peroxide to complete the digestion; and, *(ii)* a microwave-assisted closed system using concentrated nitric acid and hydrogen peroxide. The analytical performances were evaluated through the residual carbon contents. These contents were 0.358 ± 0.012% with the open system with conventional heating and 0.614 ± 0.023% with the microwave-assisted closed vessel system, demonstrating the high efficiency of both proposed procedures. The closed system was preferred because the process was faster and safer. Moreover, the accuracy determined by a recovery test was better than for the open systems. In both cases the LOD were in the sub-μg g^{-1} range. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) can be an alternative approach for the determination of trace elements in biodiesel. Woods and Fryer[49] explored the use of an ICP–MS instrument fitted with an octopole reaction system (ORS) for the elemental determination in several biofuel materials. Dilution with kerosene was used as a sample preparation procedure. The ORS removed matrix- and plasma-based spectral interferences reducing the LOD. In fact the LOD found were 0.0109 µg kg^{-1} and 0.0293 mg kg^{-1} for Be and S, respectively. Moreover, rapeseed FAME sample was spiked with a multielemental solution and recoveries for all elements went from 90 to 120%, although the majority fell within 5% of the target value, indicating reliable interference removal for the spiked matrices.

As in ICP-OES, microemulsions have been explored as an alternative sample preparation method. Amais *et al.*[110] developed a method for the determination of Cd, Co, Cu, Mn, Ni, Pb, Ti, and Zn in biodiesel microemulsified samples by ICP-MS. Microemulsions were prepared using 0.25 mL Triton X-100, 0.25 mL 20% v v−1 HNO_3, 0.50 mL biodiesel sample and 4.0 mL n-propanol. The accuracy of the method was evaluated by recovery experiments. Recoveries found were in the range 76.5 to 116.2% for all analytes and LODs were in the 9.63 10^{-3} to 19.5 µg L^{-1} range. It is important to note, that an oxygen gas flow was additionally incorporated, and as consequence, the noise of the blank signal increased. In fact, LODs without the additional oxygen gas flow were lower.

Alternative sample introduction systems

The sample introduction systems employed in the studies mentioned so far consisted of a nebulizer operated at liquid flow rates on the order of mL min^{-1} adapted to a spra y chamber. Microsample introduction systems have been considered as suitable devices for the analysis or organic samples through ICP techniques. The main advantages of these devices are: (*i)* low sample volume required to perform the analysis; *(ii)* high analyte transport efficiency; *(iii)* low plasma solvent load; *(iv)* reduction in the volume of waste generated.[128] De Souza *et al.*[129] compared the performance of a parallel path micronebulizer with that of a concentric micronebulizer for the elemental determination in biodiesel and other oils by ICP-OES. The main advantage of the parallel path micronebulizers over the conventional ones is the low risk of blockage, thus allowing the introduction of samples with high contents of dissolved solids. Moreover, limits of detection for the parallel flow nebulizer were lower than for the concentric one.

Additional systems have been used to carry out biodiesel analysis. Thus, cross-flow micronebulizers have been modified with an additional channel for the introduction of an extra liquid flow.[130,131] In this way, the organic sample is continuously introduced through one channel of the nebulizer, while aqueous calibration standards are sequentially nebulized through the other one. Aerosol droplets generated by both channels are mixed in the spray chamber and the resulting mixture reaches the ICP, thus allowing the analysis of organic samples by on-line standard addition calibration using aqueous calibration solutions. Concentric nebulizers were also used for this purpose.[132] The accuracy of the system was tested by recovery test, for all the analytes, the results were included in the range of 96-101%.

On the other hand, the spray chamber has been modified to promote the complete transport of the sample to the plasma. In this sense, Sánchez *et al.*[121] employed a 350ºC heated low inner volume single pass spray chamber to mitigate the matrix effects in the analysis of biofuel samples by ICP-OES. The results have proved that the higher the chamber walls temperature, the higher the sensitivity. As a result, limits of detection decreased below 7 µg L^{-1} for elements such as manganese, vanadium and silicon. Furthermore, memory effects were less severe as the temperature raised. Another benefit of increasing the TISIS chamber walls temperature was that matrix effects became less pronounced as compared to a Cyclonic chamber.[119–121] Thus, at 350°C non-spectral interferences were eliminated likely because the analyte transport efficiency to the plasma was close to 100% irrespective of the sample analyzed. The developed procedure was applied to the analysis of biodiesel with recoveries close to 100% for four biodiesel samples. The TISIS spray chamber and flow injection was used for the determination of nickel, vanadium and manganese in fuel and biofuel samples by

ICP-MS.[120] In this case, the amount of sample injected was only 2.5 µL. Moreover, the chamber temperature was optimized in terms of sensitivity and mitigation of matrix effects. It was found that sensitivity peaked at 110°C heating temperature. However, non-spectral interferences caused by differences in the matrix composition became less severe as this variable was increased and they were virtually eliminated at 200 °C. As a consequence, a single xylene based standard could be used as a universal standard.[133,134]

Another approach explored for the analysis of biodiesel has been to decrease the temperature of the spray chamber, thus reducing the amount of organic matter reaching the plasma. Chaves *et al.*[5] demonstrated that cooling a cyclonic spray chamber at -5°C reduced sufficiently the amount of organic solvent introduced into the plasma. Therefore, it was not necessary to introduce oxygen using ethanol and 1-propanol as a solvents. For this device, the relative standard deviation was lower than 5% and limits of detection were at the low µg g $^{-1}$ level (Table 4~~Table 3~~).

Electrothermal vaporization (ETV) can be used as an alternative approach to minimize the problems related to the use of conventional sample introduction systems.[135,136] The main advantage of this device is the separation of the analyte from the matrix sample in the pyrolysis step. As a result carbon deposits formation and some polyatomic interferences are mitigated.[137] Moreover, due to the low amount of sample introduced (*c.a.*, 20 µL) the problems related to the degradation of the plasma ionization or excitation capability are avoided. Besides, this sample introduction system allows performing a preconcentration procedure from several consecutive sample injections on the surface of the vaporizer thus improving the analytical figures of merit. Chaves *et al.*[94] developed a methodology for the determination of Co, Cu, Fe, Mn, Ni and V in emulsions of diesel and biodiesel samples by ETV-ICP-MS. Pd played two main roles; as a chemical modifier it stabilized the analytes and as a carrier this element improved the transport of the analytes from the ETV to the plasma.

The LODs were, in ng g^{-1}, 0.5 for Co, 1.5 for Cu 3 for Fe, 0.3 for Mn, 0.5 Ni, and 1 for V. Moreover, recovery tests were carried out to evaluate the accuracy of the method. This parameter was in the 80-120% range.. Recently, a tungsten filament has been employed to vaporize the analyte.[138] Advantages of this approach over conventional graphite ovens are: *(i)* it is simpler and less expensive, since it requires a single low power source; and, *(ii)* carbides formation is minimized, what is highly interesting for the determination of some elements such as silicon. In fact, this element, together with phosphorous were accurately determined. Limits of detection of 0.4 and 0.1 mg kg^{-1} were obtained for P and Si, respectively. The main drawback of ETV is the transient nature of the signal, which reduces the amounts of elements determined simultaneously.[139]

3.2.3. Isotopic Dilution Mass Spectrometry (IDMS)

One of the most challenging issues of the application of isotopic dilution is the mixture between sample and spike isotopes. The ideal scenario is a complete isotopic equilibrium between both. If the analyte and the isotopically-enriched spike are in the same species a complete mixing is sufficient to guarantee that both are being ionized with the same efficiency. This situation becomes more complicated in biofuel samples which have a very demanding matrix.

To overcome problems related with isotopic equilibration, a pre-treatment step as the digestion of the sample is required. Recently, Amais *et al.*[140] developed a method for the determination of sulphur in biodiesel by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) after sample digestion. The applied procedure involved pre-digestion and spiking of approximately 0.25 g aliquots of the samples with ^{34}S (approximately 0.25 g of a nominal 10 µg g^{-1} ^{34}S solution). For the digestion of the sample, a diluted nitric acid and hydrogen peroxide decomposition medium was used. Furthermore, medium resolution mode was employed to eliminate isobaric interferences at ^{32}S and ^{34}S caused by polyatomic phosphorus and oxygen species, as well as sulfur hydride ions. The accuracy and the precision of the method were tested by analysing a diesel certified reference material. Despite the favourable accuracy and precision of the proposed method, it did not have a limit of detection low enough to conduct S determination below 0.6 mg kg^{-1}. This was due to the magnitude of the instrument background.

One of the main drawbacks of the SF-ICP-MS is a 10-fold reduction in ion transmission efficiency and hence, in signal intensity. Moreover, the cost of this type of instruments is higher than for a quadrupole-based ICP-MS. This is why Balcaen *et.al.*[141] used a triple quadrupole (ICP-QQQ) instrument for the determination of S by isotope dilution. This system consisted in an octopole-based collision/reaction cell located between two quadrupole analyzers. The major advantage of the ICP-QQQ is the enhanced spectral resolution owing to the double mass selection in MS/MS mode and the production of chemical reactions. Thus S was detected after the conversion of S^+ ions into SO^+ ions through reaction with oxygen. As a proof-of-concept, the technique was successfully applied to the S determination in a biodiesel reference material. Moreover, LOD for this approach were in the range of µg kg^{-1}.

3.3. Analysis by additional techniques

Alternative techniques have been proposed for the determination of trace elements in biodiesel samples. In this way, FAES,[59,105,142,143] FAAS,[91,108,144–148] and ETAAS[92,94,104,106,107,109,112,149–157] have been used to quantify some alkaline metals in these samples. Other alternative techniques have been MIP-OES,[158] ionic chromatography,[159,160] capillary electrophoresis[161,162] and voltammetry.[163–168]

Flame Atomic Emission Spectrometry (FAES) could be considered as a low cost alternative for the determination of the four major elements (Ca, Na, K and Mg) in biodiesel samples. Alkalines are easily and efficiently atomized in flames.[142] A method for the determination of Na and K in biodiesel, from different vegetable oils, was proposed by Chaves *et al.*[143]. Microemulsions were prepared by mixing biodiesel samples with n-propanol and an aqueous acid solution, which allowed the use of aqueous standards for the calibration. Sample introduction through discrete aspiration or by continuous aspiration (CA) were compared, moreover, the results obtained with ICP-OES were taken as a reference. Na and K concentrations were determined and for the employed methods, the values obtained were not significantly different for a 95% confidence level. Furthermore, by comparing LOD for discrete and continuous aspiration modes, values lower than 0.1 $\mu g\ g^{-1}$ were obtained. The direct dissolution of the sample into ethanol was proposed by Barros *et al.*[105]an aqueous standards were again employed. Two different sample:solvent proportions were evaluated, 1:10 and 1:20. The limits of quantification (LOQ) in biodiesel/ethanol solution (1:20, w/v) were 4.00 and 3.60 mg kg^{-1} for Na and K, respectively. In 1:10 (w/v) biodiesel/ethanol solutions the LOQ were 2.16 and 2.00 mg kg^{-1} for Na and K, respectively. In both cases LOQs were lower than the limit established by the EN 14214 (5 mg kg^{-1}).[59] Moreover, the feasibility of the use of aqueous standards was studied by recoveries test. For both metals, the recoveries were in the range 91-108%.

Flame Atomic Absorption Spectrometry (FAAS) has been explored as an alternative to ICP techniques for the determination of K, Na, Ca and Mg in biodiesel samples. The advantage of this technique is that it is simpler, cheaper and more tolerant to organic matrices than ICP. The dilution of biodiesel sample in xylene or n-hexane is widely used as pretreatment sample step. In fact, it has been recommend by international legislation.[144–146] However, the main drawback of this technique is that organometallic standards are required, which have a low stability in solution and are expensive. Ethanol[147] was compared with xylene as solvent for the determination of Ca, K, Na and Mg in biodiesel. It was observed that the ethanolic medium provided greater sensitivity for K and Mg; whereas, for Ca and Na, similar sensitivities were obtained using both media. Because the surface tension of ethanol is lower than for xylene, the nebulization process is favored, thus increasing the mass of analyte reaching the flame. Moreover, since a higher proportion of ethanol reached the flame, compared to xylene, the flame temperature increased. In the case of Ca, a different flame was used (N_2O/C_2H_2), and the temperature increase due to the presence of the organic solvents became less significant.

As in ICP techniques, microemulsification of the sample has been applied allowing the use of aqueous standards. De Jesus *et.al.*[91] used n-pentanol, Triton X-100 and water for the microemulsion preparation. Microemulsified aqueous standards were employed. The flame composition was optimized in terms of sensitivity and the optimal C_2H_2/air ratio was 0.131. For these experimental conditions the limits of detection obtained were 0.1 $\mu g\ g^{-1}$ and 0.06 $\mu g\ g^{-1}$ for sodium and potassium, respectively. The LODs obtained were compared with those obtained following the European Standards[145,146] and higher values were found for the dilution procedure (0.2 $\mu g\ g^{-1}$ and 0.1 $\mu g\ g^{-1}$ for sodium and potassium, respectively). The same emulsifier was used by Amais *et al.*[148], whereas a different flame composition was employed. LODs were in the same range as in the previous work. Additional emulsifiers have been applied for the alkaline metals in this kind of samples. Lyra *et al.*[108] prepared the microemulsification by using HNO_3, CsCl, for sodium and potassium determination, KCl, for calcium and magnesium determination, and n-propanol.

Electrothermal atomic absorption spectrometry (ETAAS) sensitivity is 2–3 orders of magnitude higher than that of FAAS. For this reason it has been used for the analysis of some metals in petroleum samples.[104,149] The field of application of this determination technique has been extended to biodiesel samples by several research groups. Lobo *et al.*[92] developed a method for the Ni and Cd analysis using microemulsion as a sample preparation. Tungsten was employed as a chemical modifier. In a previous work, two chemical modifiers (Pd+Mg and W) and two distinct sample preparation procedures (microemulsion and wet digestion in a focused microwave system) were investigated[107] and the optimum experimental conditions corresponded to microemulsion preparation and use of W. Recoveries were measured varying from 93% to 108% for Ni and from 98% to 116% for Cd. Therefore, the accuracy was good enough for the routine analysis of these samples. The improvement of the sensitivity attainable by ETAAS and the advantages of the emulsion sample preparation, were taken for the determination of Cd and Hg in this kind of samples at µg kg^{-1} level.[150] Ghisi *et al.*[106] developed a method for the determination of Cu and Fe. The procedure for the sample preparation was its treatment with tetramethylammonium hydroxide (TMAH) as an alternative to sample dilution and emulsification. The main advantage was that the analyte was not diluted. Moreover, this treatment of the sample allowed the use of higher pyrolysis temperature eliminating the majority of the matrix before atomization thus mitigating interferences.

In order to improve LODs, de Jesus *et al.*[151] proposed direct sampling graphite furnace atomic absorption spectrometry for the determination of As and Cd. The samples were weighed directly on the solid sampling platforms and introduced into the graphite tube for analysis, thus reducing the contamination problems and increasing the sensitivity. The chemical modifier used was a mixture of 0.1% Pd + 0.06% Mg + 0.06% Triton X-100. The suitability of Pd and Mg as modifier, was previously established for petroleum.[152–154] However, the main drawback of this technique was its relatively high uncertainty (5–20% RSD). This result was explained in terms of the heterogeneity of natural samples and the small amount of sample (8 and 10 mg for As and Cd, respectively) which was introduced into the atomizer.[151]

Phosphorous determination is not commonly carried out by AAS, since its three resonance lines are in the ultraviolet vacuum (UV). Therefore, non-resonance lines (213.6 nm and 214.9 nm) should be used. As a result, poor limits of detection may be found. In order to reduce LOD, phosphorous was stabilized by adding chemical modifiers thus avoiding the formation of volatile molecular species.[155] Several modifiers were evaluated: Pd, Pd + Ca and Pd + Mg. The results showed that Pd was the best option in terms of sensitivity. The suitability of the method was evaluated by comparison with the EN 14107.[112] No significant differences were observed between the results afforded by the proposed and the standard procedures. Another important issue in the P determination affecting the LOD is that the P hollow cathode lamps are among the least intense ones. This problem could be solved by means of high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS AAS). Moreover, HR-CS AAS allowed the simultaneous observation of the P atomic lines and PO molecular bands. Again Pd-based modifiers enhanced the formation of P atoms, whereas inhibited the formation of PO molecules.[156] The advantages of this technique were demonstrated by the decrease of the LOD (0.5 $\mu g\ g^{-1}$) in comparison with the conventional ETAAS.[157] The unsurpassed background correction systems, the visualization of the entire analytical spectrum and the improvement on the LODs due to the HR-CS AAS were advantageous for the determination of Al, Cu, Fe and Mn.[109] For the improvement of the Al analytical figures of merit, a platform pre-treated with Zr as a permanent chemical modifier was employed to prevent the formation of aluminium carbide. Furthermore, different calibration approaches were used depending on the analyte. For Cu, Fe and Mn, the calibration was carried out using aqueous standards, whereas, ethanolic ones were used for

Al. LODs for Cu, Fe and Mn obtained with this approach were similar to those found for ETV-ICP-MS.[94]

A procedure for total and inorganic mercury determination in biodiesel by CV-AFS was developed by Aranda *et al*.[96] The samples were introduced directly as oil-in-water emulsions in a flow injection manifold. Mercury vapour was generated using an acidic $SnCl_2$ solution in a continuous flow system what gave a 0.2 µg kg^{-1} LOD.

Dancsak *et al.*[169] have recently employed tungsten filaments extracted from microscope light bulbs to decompose biodiesel matrix, and atomize and excite the analytes to determine sodium, potassium, chromium and vanadium by tungsten coil atomic emission spectrometry (WCAES). The accuracy was checked by determining Na and K in a biodiesel reference sample and carrying out spike experiments for Cr and V. No statistically significant differences were observed between reference and determined values for all analytes at a 95% confidence level.

Microwave-induced plasma optical emission spectrometry (MIP-OES) and a flow blurring nebulizer were used to determine silicon in diesel and biodiesel samples by Amais *et al.*[158] A simple dilution with ethanol was used as sample preparation procedure. Two additional sample preparation methods were also evaluated for comparison: closed-vessel microwave-assisted acid digestion and microemulsification. Limits of detection (LOD) vary from 5 to 20 µg L^{-1} and relative standard deviations (RSD) were lower than 2% in all cases.

Ion chromatography has been employed for the determination of elements such as Na, Ca, K, Mg[159] and P.[160] De Caland *et al.*[159] developed a method for the quantitative determination of Na^+, K^+, Mg^{2+} and Ca^{2+}. The proposed method employed water extraction, heating and ultrasound as a pre-treatment sample procedure. For comparison, the samples were also analyzed using ICP-OES with similar accuracy and precision results. Zhang *et al.*[160] developed a method to measure the content of inorganic phosphate in oil samples, by direct injection of solvent extracted oil into ion chromatography. Biodiesel oils were dissolved in acetone and an ion chromatography system with sample matrix elimination function was applied to directly determine their phosphate content against acetone based standards.

Capillary electrophoresis equipped with a diode array detector was used for the determination of Na^+, K^+, Ca^{2+}, Mg^2, using barium (Ba^{2+}) as internal standard.[161] Separation was conducted in a fused-silica capillary column with indirect UV detection at 214 nm. The method presented a good linearity in the concentration range of 0.5–20 mg kg^{-1}. The same separation technique coupled to a conductivity detector was used for the determination of the four main cations among other species (*i.e.* sulfate, phosphate, formate, acetate, propionate and glycerol).[162]

Moreover, voltammetry has been used for the determination of metal contents in biodiesel samples. A method for P quantification in the form of phosphate using a 1:12 phosphomolybdic film modified glassy carbon electrode in cyclic voltammetry was developed by Zezza *et al.*[163] Anodic stripping voltammetry has been also applied for biodiesel analysis. Pinto *et al.*[165] optimized the determination of trace levels of Cd^{+2}, Cu^{+2}, Pb^{+2} and Zn^{+2} via ASV using a bismuth film electrode. Deposition time and voltage step were the most important factors identified. The optimized method was applied to the determination of these elements in biodiesel samples after microwave digestion with diluted acid, presenting satisfactory values for accuracy and precision. A mercury film electrode was used by Martiniano *et al.*[164] to determine direct and simultaneously Pb^{+2} and Cu^{+2}. De Souza *et al.*[115] used a nickel hexacyanoferrate-modified electrode for K^+. The modified electrodes exhibited a linear response in the concentration range of 4.0×10^{-5} to 1.0×10^{-2} mol L^{-1}, with a detection limit of 1.9×10^{-5} mol L^{-1}. A chemically modified electrode with nanoparticles of nickel hexacyanoferrate was employed for the determination of potassium ions in a microemulsion of biodiesel.[114] An alternative method for the determination of calcium in biodiesel samples using square-wave voltammetry and a glassy carbon electrode in a solution containing EDTA was proposed by Almeida *et al.*[168] A microwave assisted acid digestion of the biodiesel samples was carried out before analysis. In addition, good reproducibility (CV maximum of 0.70%) and accuracy (recovery around 102%) were obtained making the method suitable for the determination of Ca^{2+} in biodiesel samples.

Table 4~~3~~. Summary of the limits of detection obtained in biodiesel samples by several authors.

Element	Technique	Conditions	LOD	Range concentration (min-max)*	Ref.
Ag	ICP-MS	EC (Kerosene,1:3)	0.149 µg kg^{-1}	0.257 – 3.15 µg kg^{-1}	49
Al	ETAAS	EC (Ethanol, 1:5 m:v) $Pd(NO_3)_2$ + $Mg(NO_3)_2$ as modifier	0.013 µg g^{-1}	0.038 – 0.443 µg g^{-1}	109
As	ICP-MS	EC (Kerosene,1:3)	0.066 µg kg^{-1}	1.02 – 1.29 µg kg^{-1}	49
	ETAAS	EC (Direct sampling) Pd + Mg + Triton X-100 as modifier	5.1 µg kg^{-1}	n.d.	151
B	ICP-MS	EC (Kerosene,1:3)	6.57 µg kg^{-1}	40.3 - 334 µg kg^{-1}	49

Ba	ICP-MS	EC (Kerosene,1:3)	0.0990 µg kg^{-1}	4.64 – 55.8 µg kg^{-1}	49
Be	ICP-MS	EC (Kerosene,1:3)	0.0109 µg kg^{-1}	0.0202 – 0.0609 µg kg^{-1}	49
Ca	ICP-OES	EC (Kerosene, 1:4)	0.4 - 9 µg kg^{-1}	2 – 10 mg kg^{-1}	4
	ICP-OES	EC (Kerosene, 1:10)	0.003 mg kg^{-1}	0.603- 401.2 mg kg^{-1}	113
	ICP-OES	EC (Kerosene, 1:10)	0.05 mg kg^{-1}	0.06 – 7.4 mg kg^{-1}	115
	ICP-OES	EC (Kerosene, 1:10)	0.04 mg kg^{-1}	0.17 – 36.3 mg kg^{-1}	117
	ICP-OES	EC (Ethanol, 1:10) IS: Y	0.03 µg g^{-1}	0.38 – 0.56 µg g^{-1}	3
	ICP-OES	EC (Ethanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.08 µg g^{-1}	0.4 – 28.5 µg g^{-1}	5
	ICP-OES	EC (1-Propanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.05 µg g^{-1}	0.4 – 28.5 µg g^{-1}	5

	ICP-OES	EC (Aqueous standards) Emulsification	0.05 µg g^{-1}	0.19 – 1.09 µg g^{-1}	124
	ICP-OES	EC (Aqueous standards) Emulsification IS: Y	0.121 mg kg^{-1}	0.27 – 0.32 mg kg^{-1}	126
	ICP-OES	EC (Open digestion) IS: Y	0.78 µg g^{-1}	n.d.	127
	ICP-OES	EC (Microwave close digestion) IS: Y	0.40 µg g^{-1}	n.d.	127
	ICP-MS	EC (Kerosene,1:3)	6.40 µg kg^{-1}	20.8 - 135 µg kg^{-1}	49
	FAAS	EC (Ethanol, 1:10 m:v))	0.31 mg kg^{-1}	0.37 – 1.30 mg kg^{-1}	147
	FAAS	EC Microemulsification	0.11 mg L^{-1}	n.d.	148
	FAAS	EC Microemulsification	0.1 µg g^{-1}	0.10 – 5.34 µg g^{-1}	108
	IC	EC (Ca^{2+})	0.23 mg kg^{-1}	0.42 – 6.64 mg kg^{-1}	159
	CE + Diode	IS	0.3 mg kg^{-1}	1.9 – 3.4 mg	161

	array detector	Liquid-liquid extraction (Ca^{2+})		kg^{-1}	
	CE + Coupled contactless conductivity detector	Liquid-liquid extraction (Ca^{2+})	0.12 mg L^{-1}	0.12 – 0.23 mg kg^{-1}	162
	Squarewave Voltammetry	Glassy carbon electrode Sample digestion Standard addition (Ca^{2+})	1.6 10-3 µmol L^{-1}	0.34 – 2.84 µmol L^{-1}	168
	HR-CS FAAS	EC (Xylene, 1:10 m:v)	0.34 mg kg^{-1}	2.09 – 2.11 mg kg^{-1}	144
	LS FAAS	EC (Xylene, 1:10 m:v)	0.52 mg kg^{-1}	2.09 – 2.11 mg kg^{-1}	144
Cd	ICP-MS	EC (Kerosene,1:3)	0.108 µg kg^{-1}	0.304 – 0.589 µg kg^{-1}	49
	ICP-MS	EC (Aqueous standards) Microemulsification	$9.63\ 10^{-3}$ - $7.77\ 10^{-2}$ µg L^{-1}	0.14 – 0.25 µg L^{-1}	110
	ETAAS	EC Microemulsification	0.1 µg L^{-1}	n.d.	92

		W as modifier			
	ETAAS	Standard addition Emulsification Pd–Mg mixture as modifier	0.3 µg kg^{-1}	4.83 µg kg^{-1}	150
	ETAAS	EC (Direct sampling) 0.1% Pd + 0.06% Mg + 0.06% Triton X-100 as modifier	0.2 µg kg^{-1}	n.d.	151
	Anodic stripping voltammetry	Bismuth film electrode Sample digestion (Cd^{2+})	2 ng L^{-1}	0.17 – 0.65 mg kg^{-1}	165
Cl	ICP-OES	EC (Kerosene, 1:4)	400 -950 µg kg^{-1}	n.d.	4
Co	ICP-MS	EC (Kerosene,1:3)	0.0337 µg kg^{-1}	0.0449 – 0.124 µg kg^{-1}	49
	ICP-MS	EC (Aqueous standards) Microemulsification	9.23 10^{-2} µg L^{-1}	5.87 – 6.11 µg L^{-1}	110
	ETV-ICP-MS (Pd as modifier)	EC	0.5 ng g^{-1}	n.d.	94

Cr	ICP-OES	EC (Kerosene, 1:10)	0.011 mg kg^{-1}	0.269 mg kg^{-1}	113
	ICP-MS	EC (Kerosene,1:3)	0.0224 µg kg$^{−1}$	0.376 – 1.36 µg kg$^{−1}$	49
	WCAES	Tungsten coil atomizer Standard addition	70 - 300 µg kg^{-1}	n.d.	169
Cu	ICP-OES	EC (Kerosene, 1:10)	0.003 mg kg^{-1}	0.118 – 0.869 mg kg^{-1}	113
	ICP-OES	EC (Ethanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.01 µg g^{-1}	0.14 – 1.62 µg g^{-1}	5
	ICP-OES	EC (1-Propanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.008 µg g^{-1}	0.14 – 1.62 µg g^{-1}	5
	ICP-OES	EC (Aqueous standards) Emulsification	0.03 µg g^{-1}	0.99 – 1.09 µg g^{-1}	124
	ICP-OES	EC (Aqueous standards) Emulsification	0.008 mg kg^{-1}	<0.008 – 0.303 mg kg^{-1}	126

		IS: Y			
	ICP-MS	EC (Kerosene,1:3)	0.0264 µg kg^{-1}	0.730 – 11.5 µg kg^{-1}	49
	ICP-MS	EC (Kerosene,1:3)	0.101 µg kg^{-1}	0.730 – 11.5 µg kg^{-1}	49
	ICP-MS	EC (Aqueous standards) Microemulsification	5.13 - 5.47 µg L^{-1}	n.d.	110
	ETV-ICP-MS (Pd as modifier)	EC	1.5 ng g^{-1}	13.8 - 142 ng g^{-1}	94
	ETAAS	EC (Treatment with tetramethylammonium hydroxide) 0.1% Pd + 0.06% Mg + 0.06% Triton $X^{-1}00$ as modifier	15 ng g^{-1}	130 - 182 ng g^{-1}	106
	ETAAS	EC (Ethanol, 1:5 m:v) $Pd(NO_3)_2$ + $Mg(NO_3)_2$ as modifier	0.009 µg g^{-1}	0.010 – 0.194 µg g^{-1}	109
	Anodic stripping voltammetry	Mercury- film electrode Microemulsification	4.69 10^{-9} mol L^{-1}	n.d.	164

		Standard addition (Cu^{2+})			
	Anodic stripping voltammetry	Bismuth film electrode Sample digestion (Cu^{2+})	12 ng L^{-1}	0.37 – 1.10 mg kg^{-1}	165
Fe	ICP-OES	EC (Kerosene, 1:10)	0.011 mg kg^{-1}	0.104 – 17.12 mg kg^{-1}	113
	ICP-OES	EC (Ethanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.01 µg g^{-1}	0.78 – 21.2 µg g^{-1}	5
	ICP-OES	EC (1-Propanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.01 µg g^{-1}	0.78 – 21.2 µg g^{-1}	5
	ICP-OES	EC (Aqueous standards) Emulsification	0.01 µg g^{-1}	0.04 – 1.09 µg g^{-1}	124
	ICP-OES	EC (Aqueous standards) Emulsification IS: Y	0.006 mg kg^{-1}	0.029 – 2.200 mg kg^{-1}	126

	ICP-MS	EC (Kerosene,1:3)	0.0869 µg kg^{-1}	4.61 – 50.8 µg kg^{-1}	49
	ETV-ICP-MS (Pd as modifier)	EC	3 ng g^{-1}	120 - 375 ng g^{-1}	94
	ETAAS	EC (Treatment with tetramethylammonium hydroxide) 0.1% Pd + 0.06% Mg + 0.06% Triton X-100 as modifier	24 ng g^{-1}	86 - 4940 ng g^{-1}	106
	ETAAS	EC (Ethanol, 1:5 m:v) Pd(NO3)2 + Mg(NO3)2 as modifier	0.006 µg g^{-1}	0.023 – 5.18 µg g^{-1}	109
Hg	ICP-MS	EC (Kerosene,1:3)	0.123 µg kg^{-1}	0.396 – 0.791 µg kg^{-1}	49
	ETAAS	Standard addition Emulsification Pd–Mg mixture as modifier	10.2 µg kg^{-1}	23.2 µg kg^{-1}	150
	FI-CV-AAS	Emulsification	0.2 µg kg^{-1}	0.5 – 3.7 µg kg^{-1}	96
K	ICP-OES	EC (Kerosene, 1:4)	7.1 µg kg^{-1}	5 – 10 mg kg^{-}	4

				1	
	ICP-OES	EC (Kerosene, 1:10)	0.070 mg kg^{-1}	2.059- 32.46 mg kg^{-1}	[113]
	ICP-OES	EC (Kerosene, 1:10)	0.1 mg kg^{-1}	n.d.	[115]
	ICP-OES	EC (Kerosene, 1:10)	0.8 mg kg^{-1}	n.d.	[117]
	ICP-OES	EC (Ethanol, 1:10) IS: Y	0.3 µg g^{-1}	1.3 – 6.0 µg g^{-1}	[3]
	ICP-OES	EC (Ethanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.4 µg g^{-1}	17.5 - 189 µg g^{-1}	[5]
	ICP-OES	EC (1-Propanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.2 µg g^{-1}	17.5 - 189 µg g^{-1}	[5]
	ICP-OES	EC (Aqueous standards) Emulsification IS: Y	0.241 mg kg^{-1}	n.d.	[126]
	ICP-OES	EC (Open digestion) IS: Y	0.11 µg g^{-1}	2.1 – 7.3 µg g^{-1}	[127]
	ICP-OES	EC (Microwave close digestion)	0.16 µg g^{-1}	2.1 – 7.3 µg g^{-1}	[127]

		IS: Y			
	ICP-MS	EC (Kerosene,1:3)	2.10 µg kg^{-1}	15.4 – 50.6 µg kg^{-1}	[49]
	FAES	EC Microemulsification	0.06 - 0.09 µg g^{-1}	2.00 – 63.76 µg g^{-1}	[143]
	FAES	EC (Ethanol, 1:10 and 1:20)	0.60 mg kg^{-1} (1:10) 1.08 mg kg^{-1} (1:20)	n.d.	[105]
	FAAS	EC (Ethanol, 1:10 m:v))	0.17 mg kg^{-1}	2.7 – 7.2 mg kg^{-1}	[147]
	FAAS	EC (Aqueous standards) Microemulsification	0.06 µg g^{-1}	0.71 – 36.2 mg kg^{-1}	[91]
	FAAS	EC Microemulsification	0.01 µg g^{-1}	0.13 – 2.30 µg g^{-1}	[108]
	IC	EC (K^+)	0.42 mg kg^{-1}	0.35 – 0.91 mg kg^{-1}	[159]
	CE + Diode array detector	IS Liquid-liquid extraction (K^+)	0.3 mg kg^{-1}	1.1 -16.8 mg kg^{-1}	[161]
	CE + Coupled	Liquid-liquid	0.12 mg L^{-1}	0.46 – 0.61	[162]

	contactless conductivity detector	extraction (K^+)		mg kg^{-1}	
	Voltammetry	Glassy carbon electrode modified with nickel(II) hexacyanoferrate nanoparticles Microemulsification Standard addition (K^+)	5.0 10-5 mol L^{-1}	12.9 mg kg^{-1}	[166]
	Voltammetry	Nickel hexacyanoferrate-modified electrode Liquid-liquid extraction (K^+) Standard addition	1.9 10-5 mol L^{-1}	0.96 mg kg^{-1}	[167]
	HR-CS FAAS	EC (Xylene, 1:10 m:v)	0.023 mg kg^{-1}	9.20 – 10.00 mg kg^{-1}	[144]
	LS FAAS	EC (Xylene, 1:10 m:v)	0.57 mg kg^{-1}	9.20 – 10.00 mg kg^{-1}	[144]
	WCAES	Tungsten coil atomizer	70-80 µg kg^{-1}	10.8 – 95.6 mg kg^{-}	[169]

		Standard addition		1	
Mg	ICP-OES	EC (Kerosene, 1:4)	0.9 -39 µg kg^{-1}	1 – 10 mg kg^{-1}	4
	ICP-OES	EC (Kerosene, 1:10)	0.009 mg kg^{-1}	0.353 – 27.31 mg kg^{-1}	113
	ICP-OES	EC (Kerosene, 1:10)	0.01 mg kg^{-1}	0.63 – 3.6 mg kg^{-1}	115
	ICP-OES	EC (Kerosene, 1:10)	0.02 mg kg^{-1}	0.10 – 22.1 mg kg^{-1}	117
	ICP-OES	EC (Ethanol, 1:10) IS: Y	0.005 µg g^{-1}	0.058 – 5.9 µg g^{-1}	3
	ICP-OES	EC (Ethanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.001 µg g^{-1}	0.06 – 33.80 µg g^{-1}	5
	ICP-OES	EC (1-Propanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.001 µg g^{-1}	0.06 – 33.80 µg g^{-1}	5
	ICP-OES	EC (Aqueous standards) Emulsification	0.002 µg g^{-1}	0.007 – 1.08 µg g^{-1}	124
	ICP-OES	EC (Aqueous	0.006 mg	0.030 – 0.033	126

		standards) Emulsification IS: Y	kg^{-1}	mg kg^{-1}	
	ICP-OES	EC (Open digestion) IS: Y	0.04 µg g^{-1}	n.d.	127
	ICP-OES	EC (Microwave close digestion) IS: Y	0.03 µg g^{-1}	n.d.	127
	ICP-MS	EC (Kerosene,1:3)	8.65 µg kg^{-1}	6.16 – 12.1 µg kg^{-1}	49
	FAAS	EC (Ethanol, 1:10 m:v))	0.05 mg kg^{-1}	0.068 mg kg^{-1}	147
	FAAS	EC Microemulsification	0.03 mg L^{-1}	n.d.	148
	FAAS	EC Microemulsification	0.004 µg g^{-1}	0.041- 0.52 µg g^{-1}	108
	IC	EC (Mg^{2+})	0.36 mg kg^{-1}	0.06 – 0.93 mg kg^{-1}	159
	CE + Diode array detector	IS Liquid-liquid extraction (Mg^{2+})	0.3 mg kg^{-1}	n.d.	161
	CE + Coupled	Liquid-liquid	0.07 mg L^{-1}	0.28 mg kg^{-1}	162

	contactless conductivity detector	extraction (Mg^{2+})			
	HR-CS FAAS	EC (Xylene, 1:10 m:v)	0.057 mg kg^{-1}	0.47 - 0.59 mg kg^{-1}	144
	LS FAAS	EC (Xylene, 1:10 m:v)	0.11 mg kg^{-1}	0.47 - 0.59 mg kg^{-1}	144
Mn	ICP-OES	EC (Aqueous standards) Emulsification	0.005 µg g^{-1}	1.00 – 1.08 µg g^{-1}	124
	ICP-OES	EC (Aqueous standards) Emulsification IS: Y	0.001 mg kg^{-1}	0.001 mg kg^{-1}	126
	ICP-MS	EC (Kerosene,1:3)	0.0563 µg kg$^{−1}$	0.114 – 0.450µg kg$^{−1}$	49
	ICP-MS	EC (Aqueous standards) Microemulsification	7.51 10^{-1} µg L^{-1}	<0.75 – 1.23 µg L^{-1}	110
	ICP-MS	EC	Room temperature (Spray chamber):	0.22 – 0.24 µg L^{-1}	120

			0.31 ng mL^{-1} 110ºC (Spray chamber): 0.06 ng mL^{-1} 200ºC (Spray chamber): 0.23 ng mL^{-1}		
	ETV-ICP-MS (Pd as modifier)	EC	0.3 ng g^{-1}	4.9 - 76 ng g^{-1}	[94]
	ETAAS	EC (Ethanol, 1:5 m:v) $Pd(NO_3)_2 + Mg(NO_3)_2$ as modifier	0.003 µg g^{-1}	0.004 - 0.037 µg g^{-1}	[109]
Mo	ICP-MS	EC (Kerosene,1:3)	0.371 µg kg^{-1}	n.d.	[49]
Na	ICP-OES	EC (Kerosene, 1:4)	1.4 – 1.6 µg kg^{-1}	2 - 10 mg kg^{-1}	[4]
	ICP-OES	EC (Kerosene, 1:10)	0.019 mg kg^{-1}	1.414- 21.59 mg kg^{-1}	[113]
	ICP-OES	EC (Kerosene, 1:10)	0.1 mg kg^{-1}	0.6 - 23 mg kg^{-1}	[115]

	ICP-OES	EC (Kerosene, 1:10)	0.2 mg kg^{-1}	0.23 – 13.8 mg kg^{-1}	117
	ICP-OES	EC (Ethanol, 1:10) IS: Y	0.1 µg g^{-1}	1.4 – 44.3 µg g^{-1}	3
	ICP-OES	EC (Ethanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.1 µg g^{-1}	0.9 – 29.0 µg g^{-1}	5
	ICP-OES	EC (1-Propanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.1 µg g^{-1}	0.9 – 29.0 µg g^{-1}	5
	ICP-OES	EC (Aqueous standards) Emulsification	0.04 µg g^{-1}	0.14 – 1.08 µg g^{-1}	124
	ICP-OES	EC (Aqueous standards) Emulsification IS: Y	0.071 mg kg^{-1}	0.022 – 1.490 mg kg^{-1}	126
	ICP-OES	EC (Open digestion) IS: Y	0.56 µg g^{-1}	6.5 – 7.6 µg g^{-1}	127
	ICP-OES	EC (Microwave close digestion)	0.16 µg g^{-1}	6.5 – 7.6 µg g^{-1}	127

		IS: Y			
	ICP-MS	EC (Kerosene,1:3)	1.19 µg kg^{-1}	127 - 1430 µg kg^{-1}	49
	FAES	EC Microemulsification	0.08 - 0.10 µg g^{-1}	3.60 – 3.73 µg g^{-1}	143
	FAES	EC (Ethanol, 1:10 and 1:20)	0.65 mg kg^{-1} (1:10) 1.20 mg kg^{-1} (1:20)	n.d.	105
	FAAS	EC (Ethanol, 1:10 m:v))	0.14 mg kg^{-1}	0.60 – 2.70 mg kg^{-1}	147
	FAAS	EC (Aqueous standards) Microemulsification	0.1 µg g^{-1}	0.5 – 39.7 mg kg^{-1}	91
	FAAS	EC Microemulsification	0.1 µg g^{-1}	1.18 – 1.51 µg g^{-1}	108
	IC	EC (Na^{+})	0.11 mg kg^{-1}	0.99 – 3.56 mg kg^{-1}	159
	CE + Diode array detector	IS Liquid-liquid extraction (Na^{+})	0.3 mg kg^{-1}	2.3 – 39.6 mg kg^{-1}	161
	CE + Coupled	Liquid-liquid	0.14 mg L^{-1}	0.97 mg kg^{-1}	162

	contactless conductivity detector	extraction (Na^+)			
	HR-CS FAAS	EC (Xylene, 1:10 m:v)	0.10 mg kg^{-1}	0.54 – 0.98 mg kg^{-1}	144
	LS FAAS	EC (Xylene, 1:10 m:v)	0.23 mg kg^{-1}	0.54 – 0.98 mg kg^{-1}	144
	WCAES	Tungsten coil atomizer Standard addition	20 µg kg^{-1}	6.08 – 41.3 mg kg^{-1}	169
Ni	ICP-OES	EC (Kerosene, 1:10)	0.006 mg kg^{-1}	0.220 – 0.948 mg kg^{-1}	113
	ICP-MS	EC (Kerosene,1:3)	0.126 µg kg^{-1}	0.397 – 3.64 µg kg^{-1}	49
	ICP-MS	EC (Aqueous standards) Microemulsification	19.3 – 19.5 µg L^{-1}	n.d.	110
	ICP-MS	EC	Room temperature (Spray chamber): 0.22 ng mL^{-1} 110ºC	1.15 – 1.17 µg L^{-1}	120

			(Spray chamber): 0.07 ng mL^{-1} 200ºC (Spray chamber): 0.18 ng mL^{-1}		
	ETV-ICP-MS (Pd as modifier)	EC	0.5 ng g^{-1}	6.5 – 14.1 ng g^{-1}	[94]
	ETAAS	EC Microemulsification W as modifier	0.9 µg L^{-1}	0.2 – 2.4 µg g^{-1}	[92]
P	ICP-OES	EC (Kerosene, 1:4)	32 -67 µg kg^{-1}	n.d.	[4]
	ICP-OES	EC (Kerosene, 1:10)	0.023 mg kg^{-1}	0.799 – 223.8 mg kg^{-1}	[113]
	ICP-OES	EC (Kerosene, 1:10)	0.09 mg kg^{-1}	1.2 – 7.6 mg kg^{-1}	[115]
	ICP-OES	EC (Kerosene, 1:10)	0.4 mg kg^{-1}	0.07 – 26.3 mg kg^{-1}	[117]
	ICP-OES	EC (Ethanol, 1:10) IS: Y	0.5 µg g^{-1}	2.8 – 7.9 µg g^{-1}	[3]

	ICP-OES	EC (Ethanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.1 µg g^{-1}	0.6 – 321.0 µg g^{-1}	5
	ICP-OES	EC (1-Propanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.1 µg g^{-1}	0.6 – 321.0 µg g^{-1}	5
	ICP-OES	EC (Aqueous standards) Emulsification	0.20 µg g^{-1}	0.96 -1.09 µg g^{-1}	124
	ICP-OES	EC (Open digestion) IS: Y	0.22 µg g^{-1}	n.d.	127
	ICP-OES	EC (Microwave close digestion) IS: Y	0.40 µg g^{-1}	n.d.	127
	ICP-MS	EC (Kerosene,1:3)	22.7 µg kg^{-1}	21.4 - 2120 µg kg^{-1}	49
	ETV-ICP-MS (Tungsten coil electrothermal matrix decompositio	EC	0.4 mg kg^{-1}	0.51 – 5.75 mg kg^{-1}	138

	n)				
	ETAAS	EC (Direct sampling) 20 µL of Pd (1000 µg mL^{-1}) in 0.1% HNO3 and 0.025% Triton X-100 as modifier	1.2 µg g^{-1}	2.4 -4.5 µg g^{-1}	155
	ETAAS	EC (Direct sampling) 30 µg Pd(NO$_3$)$_2$+ 20 µg Mg(NO$_3$)$_2$ mixture dissolved in 0.2% HNO$_3$ and 0.1% Triton X-100 as modifier	0.5 µg g^{-1}	4.2 – 4.86 mg kg^{-1}	157
	IC	EC (PO$_4^{3-}$)	0.1 mg kg^{-1}	33 -417 mg kg^{-1}	160
	Cyclic voltammetry	1:12 Phosphomolybdic modified electrode Liquid-liquid extraction Standard addition	8.7 10-6 mol L^{-1}	1.36 mg kg^{-1}	163
Pb	ICP-MS	EC (Kerosene,1:3)	0.0226 µg kg^{-1}	0.0450 – 0.385 µg kg^{-1}	49
	ICP-MS	EC (Aqueous	1.49 10^{-1} µg	<0.15 – 0.401	110

		standards) Microemulsification	L^{-1}	µg L^{-1}	
	Anodic stripping voltammetry	Mercury- film electrode Microemulsification Standard addition (Pb^{2+})	2.91 10-9 mol L^{-1}	n.d.	164
	Anodic stripping voltammetry	Bismuth film electrode Sample digestion (Pb^{2+})	8 ng L^{-1}	0.39 -2.20 mg kg^{-1}	165
S	ICP-OES	EC (Kerosene, 1:10)	0.01 mg kg^{-1}	0.6 – 0.9 mg kg^{-1}	115
	ICP-OES	EC (Ethanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.4 µg g^{-1}	1.4 - 817 µg g^{-1}	5
	ICP-OES	EC (1-Propanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.3 µg g^{-1}	1.4 - 817 µg g^{-1}	5
	ICP-OES	EC (Aqueous standards)	0.21 - 0.80 mg L^{-1}	2-7 mg L^{-1}	125

		Microemulsification			
	ICP-MS	EC (Kerosene,1:3)	0.0293 µg kg^{-1}	1.29 – 18.9 mg kg^{-1}	49
	SF-ICP-MS	ID Sample digestion	7.42 mg kg^{-1}	0.7 mg kg^{-1}	140
	ICP-MS/MS	ID Dilution (Ethanol)	0.5 -2.0 µg kg^{-1}	7.231 µg g^{-1}	141
Sb	ICP-MS	EC (Kerosene,1:3)	0.0395 µg kg^{-1}	0.0528 – 0.399 µg kg^{-1}	49
Si	ICP-OES	EC (Aqueous standards) Emulsification IS: Y	0.024 mg kg^{-1}	0.34 – 0.40 mg kg^{-1}	126
	ICP-MS	EC (Kerosene,1:3)	7.44 µg kg^{-1}	6.02 - 8220 µg kg^{-1}	49
	ICP-OES	EC	Room temperature (Spray chamber): 3-26 µg L^{-1} 200ºC (Spray chamber):	n.d.	121

			4.2 µg L^{-1} 350ºC (Spray chamber): 1.3-3 µg L^{-1}		
	ETV-ICP-MS (Tungsten coil electrothermal matrix decomposition)	EC	0.1 mg kg^{-1}	0.22 – 0.57 mg kg^{-1}	[138]
	MIP-OES	EC Sample digestion	20 – 240 µg L^{-1}	n.d.	[158]
	MIP-OES	EC (Aqueous standards) Microemulsification	5 µg L^{-1}	n.d.	[158]
Sn	ICP-MS	EC (Kerosene,1:3)	0.411 µg kg^{-1}	0.138 - 131 µg kg^{-1}	[49]
Sr	ICP-MS	EC (Kerosene,1:3)	0.0631 µg kg^{-1}	0.339 – 4.59 µg kg^{-1}	[49]
Ti	ICP-MS	EC (Kerosene,1:3)	0.706 µg kg^{-1}	0.342 – 8.08 µg kg^{-1}	[49]
	ICP-MS	EC (Aqueous	12.8 µg L^{-1}	145.8 - 180	[110]

		standards) Microemulsification		µg L^{-1}	
V	ICP-MS	EC (Kerosene,1:3)	0.0409 µg kg^{-1}	0.186 – 1.36 µg kg^{-1}	49
	ICP-MS	EC	Room temperature (Spray chamber): 0.17 ng mL^{-1} 110ºC (Spray chamber): 0.06 ng mL^{-1} 200ºC (Spray chamber): 0.08 ng mL^{-1}	1.30 – 1.40 µg L^{-1}	120
	ETV-ICP-MS (Pd as modifier)	EC	1 ng g^{-1}	n.d.	94
	WCAES	Tungsten coil atomizer Standard addition	90 - 500 µg kg^{-1}	n.d.	169

W	ICP-MS	EC (Kerosene,1:3)	0.0177 μg kg^{-1}	0.0181 – 0.121 μg kg^{-1}	49
Zn	ICP-OES	EC (Kerosene, 1:10)	0.011 mg kg^{-1}	0.099 – 2.4 mg kg^{-1}	113
	ICP-OES	EC (Ethanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.08 μg g^{-1}	1.0 – 9.1 μg g^{-1}	5
	ICP-OES	EC (1-Propanol, 1:10 for vegetable oil and 1:20 biodiesel) IS: Y	0.05 μg g^{-1}	1.0 – 9.1 μg g^{-1}	5
	ICP-MS	EC (Kerosene,1:3)	0.211 μg kg^{-1}	2.8 – 27.4 μg kg^{-1}	49
	ICP-MS	EC (Aqueous standards) Microemulsification	4.22 – 4.25 μg L^{-1}	64.7 – 184.3 μg L^{-1}	110
	FAAS	EC Microemulsification	0.08 mg L^{-1}	0.49 – 0.68 mg L^{-1}	148
	Anodic stripping voltammetry	Bismuth film electrode Sample digestion (Zn^{2+})	18 ng L^{-1}	2.3 – 4.0 mg kg^{-1}	165

n.d.: non determined in real samples

*This range corresponds to the minimum and maximum concentrations found for a given analyte and analytical method for several samples. A single figure is included when only a samples was analyzed.

3.4. Comparison among techniques

As it has been discussed throughout the previous sections, different approaches have been developed for the determination of trace elements in biodiesel samples. Because metal concentration in biodiesel samples (Table 4~~Table 3~~) is usually low, the selection of the determination technique could be considered as one of the most challenging steps.[104] Figure 4 summarizes the techniques employed for the determination of several metals in biodiesel samples.

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The included data have been calculated taken in account the data shown in Table 4~~Table 3~~ according to:

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$$\boldsymbol{Freq.use\ technique\ A}\ (\%) = \frac{\boldsymbol{studies\ by\ technique\ A\ for\ element\ X}}{\sum \boldsymbol{studies\ by\ all\ the\ techniques\ for\ element\ X}} \times \mathbf{100} \quad \textbf{Equation 2}$$

As Figure 3~~Figure 4~~ shows, ICP-OES and ICP-MS are the most employed techniques in the researches related with biodiesel analysis. Some studies dialing with FAAS determinations also appeared. Spectral interferences for AAS are minimized compared with other techniques, whereas sample throughput and limits of detection are favourable for ICP techniques. This figure algo shows the total number of studies related with the determination of each one of the elements considered. As expected, the most studied ones are Na, K, Ca, Mg, P and Cu.

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Chromatographic techniques have been developed for the determination of the alkaline elements. However, because LODs are slightly higher than those found with spectrometric techniques they have been mainly used for the determination of alkalines. Cu, Fe, Mn and Zn are expected to be found at sub-mg kg^{-1} or even µg kg^{-1} level, for that reason, ICP techniques have been extensively applied. It is important to note that since Cu and Zn are redox active, voltammetry has been proposed as alternative.

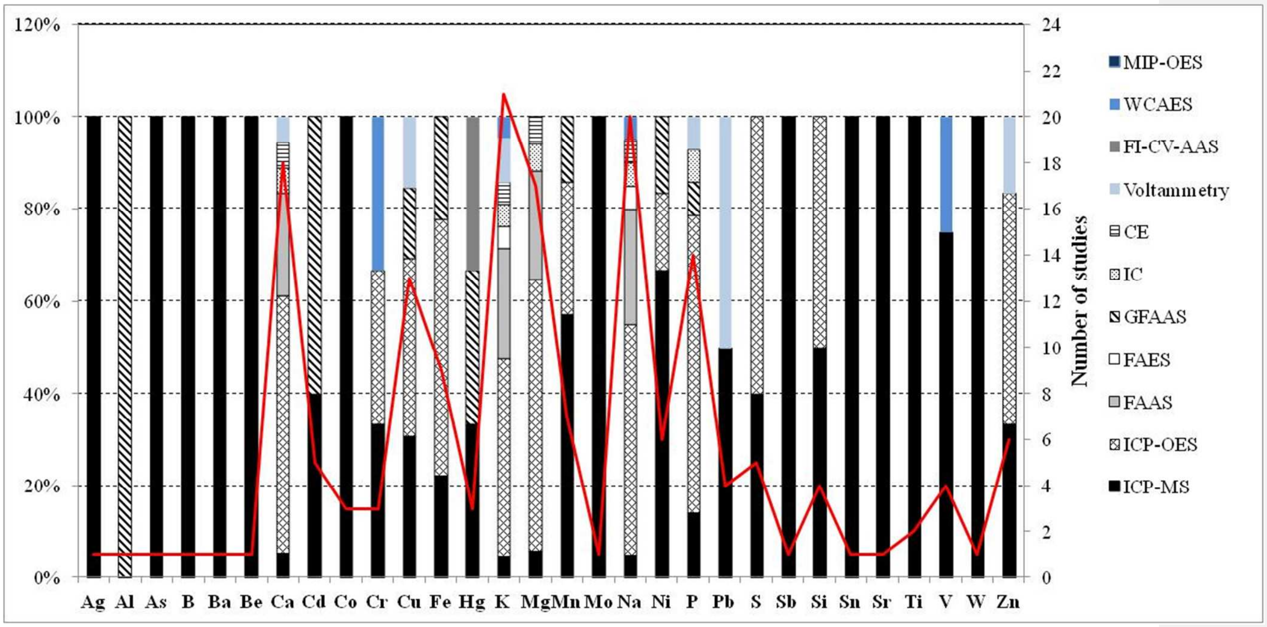

Figure 34. Techniques employed for the determination of several metals in biodiesel samples (bars) and number of studies dealing with the determination of each one of the elements (red line).

3.5. Standards for the analysis of biodiesel

Several test methods have been proposed to perform the elemental determination in biodiesel samples. For example, the European Standard EN 14214[59] describes the requirements and test methods for FAME analysis, the most common type of biodiesel, whereas, the ASTM D6751-08[60] details specifications for biodiesels blended with middle distillate fuels. Both standards establish the determination of Ca, Mg, K, Na, S and P.

Table 5~~Table 5~~ summarizes the Standards dealing with the elemental determination in biodiesel samples. This table also includes the analytical techniques recommended by each one of those Standards. If this information is compared with that included in Figure 3~~Figure 4~~ it may be concluded that ICP-MS is not yet considered. This is likely due to the fact that the elements determined by the Standards are the most abundant in biodiesel samples (Na, K, Ca and Mg) at levels that fit perfectly with the LODs afforded by techniques such as FAAS or ICP-OES. Because sulfur determination through ICP-OES and ICP-MS presents problems related with the different response as a function of the analyte chemical form, XRF techniques are often recommended by the corresponding Standards.

Table 5. List of standards for the elemental determination of biodiesel samples.

Standard reference	**Standard title/ Scope**	**Determined elements**	**Analytical technique**	**Year**
ASTM D7039	Standard Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength	S	MWDXRF	2013

	Dispersive X-ray Fluorescence Spectrometry			
EN 14107	Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of phosphorus content by inductively coupled plasma (ICP) emission spectrometry	P	ICP-OES	2003
EN 14108	Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of sodium content by atomic absorption spectrometry	Na	FAAS	
EN 14109	Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) -	K	FAAS	2003

	Determination of potassium content by atomic absorption spectrometry			
EN 14538	Fat and oil derivatives - Fatty acid methyl ester (FAME) - Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES)	Ca, Mg, Na, K	ICP-OES	2006
ASTM D6751	Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels	Specifications*		2012
ASTM D7467	Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6	Specifications*		2013

	to B20)			
prEN16709	Automotive fuels - High FAME diesel fuel (B20 or B30) - Requirements and test methods	Specifications*		2014
*These standards refer to :				
ASTM D4294 (S by EDXRF)		S	EDXRF	2010
ASTM D2622 (S by WDXRF)		S	WDXRF	2010
ASTM D7039 (S by MWDXRF)		S	MWDXRF	2013
ASTM D4951 (P by ICP-OES)		P	ICP-OES	2009
EN 14538 (Ca, Mg, K and Na by ICP-OES)		Ca, Mg, Na, K	ICP-OES	2006

4. Bioethanol

Bioethanol is refered to as ethanol obtained through carbohydrates fermentation from a wide renewable feedstock (e.g. sugar cane, corn and switchgrass) using various types of microorganisms.[1,170]

Bioethanol can be employed directly or mixed in several concentrations with unlead gasoline (e.g. E85 ethanol fuel is a mixture of 85% of bioethanol and 15% of gasoline).[170] This kind of mixture bioethanol-gasoline is known as fuel ethanol. Modifications in the engine are not required up to E10, whereas higher concentrations of ethanol are appropriate for flex-fuel engines.[170]

Bioethanol and fuel ethanol show several advantages against fossil fuels as: *(i)* A reduction of greenhouse emissions down to 65% lower than petroleum products;[170,171] *(ii)* ethanol is an oxygenated additive which improves the octane rating of fuels; and, *(iii)* burning is clean and therefore toxicity of the generated compounds is low.[170] For these reasons the production of fuel ethanol and bioethanol is growing with the simultaneous increase in the research related with the production and characterization of these new fuels. The research in fuel ethanol production and characteritzation was developed in the 70s whereas the production of research documents dealing with bioethanol virtually started at the beginnig of the XXI century. In both cases the number of papers per year has exponentially increased along the last 15 years up to more than 1000 research documents a year.

4.1. Synthesis and presence of metals. Importance of their determination.

Several materials have been employed to produce bioethanol.[171–173] Synthesis process depends strongly on the raw material. First generation bioethanol is produced from foodstuffs such as beet, sugarcane, cereal grain or corn, among others.[1] Meanwhile, second generation bioethanol generates from wood or straw and it is also known as "lignocellulosic bioethanol".[1,171]

The production of bioethanol includes four main steps (Figure 4~~Figure 5~~): *(i)* physico-chemical structure break up of the raw material; *(ii)* enzymatic hydrolisis of cellulose to monomeric sugars; *(iii)* conversion of these sugars to ethanol by fermentation; *(iv)* separation of ethanol from the fermentation broth by distilation generally followed by a final dehydratation.[171]

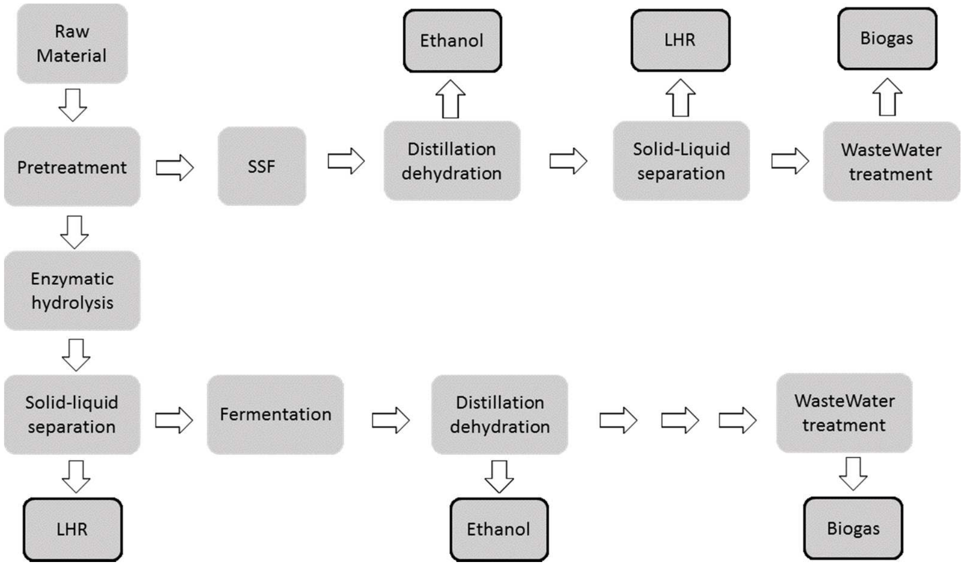

Figure 4~~5~~. General flow chart of bioethanol production process from lignocelulosic biomass (second generation). SSF: Simultaneous Saccharification and Fermentation; LHR: solid Lignin Hydrolysate Residue. Taken from[171].

At the end of the proccess either anhydrous ethanol (content of water lower than 0.7%) or hydrated ethanol (content of water from 2 to 7%) can be obtained.[174] The final product also may contain up to roughly 300 compounds depending on the origin of the raw material and the applied treatment.[1] Compounds such as alcohols (methanol, 1-propanol, isopropanol, 1-butanol, 2-butanol, etc), esters (ethyl formate, ethyl acetate, etc), ketones, aldehydes can be present. This fact together with the low metals content can hinder their quantification in bioethanol or fuel ethanol samples.

It is difficult to establish the source of metals in bioethanol. The first one can be the raw material.[2,175–177] Thus the metal content depends on the soil where raw material has grown as well as on the atmospheric pollution.[177] Concentrations on the order of mg kg^{-1} have been found in biomass for 26 elements (Sr, Ba, F, Cl, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, Zn, Cd, Hg, Al, Sn, Pb, B, As, Sb, S, Se, Te and P). Meanwhile, the content of elements such as Na, K, Ca, Mg and Si in products frequently used to obtain bioethanol can be as high as g kg^{-1}.[2] Moreover, bioethanol may be contaminated with metals during its synthesis.[175,176,178] Several metals can also appear during the fuel storage and transport in metallic containers.[175–179] Finally, some metallic species can be used as additives to promote the combustion process.[180] Obviously, when a blend is considered (*e.g.*, ethanol fuel) metals and metalloids come mainly from gasoline.[119]

As it has been previously mentioned, metals and other trace elements are present at very low concentrations in bioethanol and fuel ethanol. However, their determination is important for several reasons: *(i)* they can cause catalyst deactivation in the bioethanol transformation process[1] (e.g. sulfur impurities) and in industrial process;[175,177] *(ii)* some metals such as As, Cd, Hg, Tl or Pb cause health problems even at low concentrations;[177,181] *(iii)* others, Fe and Cu, cause damage of the vehicle engine;[175,177,178,182–185] *(iv)* heavy metals have an environmental risk;[178,180,185,186] and, *(v)* some elements preclude the stability of the bioethanol or fuel ethanol (e.g. Cu can catalyze the oxidation of gasoline in presence of alcohol).[177,178,183,187]

4.2. Analysis by ICP techniques

4.2.1. Conventional sample introduction systems and electrothermal vaporization

Several authors have reported non-spectral interferences when ethanol or other alcohols are analyzed by ICP techniques. Thus, an enhancement in the signal is observed for ethanol as compared to water.[10,14,22,23,30,41,184,186,189] For example, McCrindle *et al.*[22] reported such a change in ICP-OES sensitivity for Cd and Fe. In the case of Fe this fact caused a decrease in

LOD, in presence of ethanol. However for Cd the limit of detection was lower for pure water than for this alcohol.

In another study developed by the same authors the LODs, sensitivity and the background equivalent concentration (BEC) were determined for Pb, Cd, Al, Cr, Fe, Na, Mn, Mo and V in presence and in absence of ethanol. They observed that the operating conditions played a very important role. For a 0.6 L min^{-1} nebulizer gas flow rate and 1.36 kW RF power, the sensitivity for all analytes increased with ethanol concentration by a factor that depended on the element. In contrast, for a 0.4 L min^{-1} flow rate the addition of ethanol did not improve the sensitivity for almost all the analytes and it decreased for some elements such as Na and Al.[23]

On the other hand, some authors reported that the presence of ethanol into the plasma caused an increase in the background signal.[20,21,23] According to McCrindle *et al.*[14,23] the enhancement in terms of sensitivity was similar to that in terms of background intensity.[23] The same effect was observed for 95% ethanol solutions, the LOD were similar to pure water although the sensitivity for 95% ethanol solution was between 2 and 5 times higher than for water.[14]

Saint´Pierre *et al.*[186] studied the effect of ethanol on sensitivity for 15 elements (V, Mn, Co, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Cd, Tl, Pb and Bi) in ICP-MS and they reported that the signal in presence of ethanol was from 15 to 25 times higher than the signal for plain water solutions depending on the isotope. These findings were in concordance with the results obtained by Dressler *et al.*[41] who evaluated the effect of methanol, ethanol and isopropanol in ICP-MS for 13 elements (As, Ba, Bi, Cd, Ce, Cu, Hg, In, Pb, Rh, Se, Tl and U). On the other hand, Rocha *et al.*[184] reported that for copper and iron 7% of water in hydrated fuel ethanol (HFE) induced a 30% signal decrease with respect to anhydrous fuel ethanol (AFE).

Sample treatment methods

Several studies recommend ethanol or fuel ethanol dilution with an appropriate solvent.[37,38,186,190] For this kind of samples, water is the most widely employed, [37,38,186,190] although other solvents can be employed to dilute these type of samples.[37] The choice of the solvent may affect the method sensitivity, precision and accuracy. Thus, using a programmable temperature spray chamber, it has been verified that the sensitivity in isopropanol is from three to four times higher than that in methanol.[191] However, an obvious limitation of sample dilution is that LODs and sensitivities are severely degraded.

Overcoming non spectral interferences

Besides sample dilution, several methods have been developed in order to overcome non spectral interferences caused by ethanol, among them: *(i)* matrix matching; *(ii)* internal standardization; and, *(iii)* isotopic dilution.

As regards matrix matching Rocha *et al*.[184] prepared the standards in ethanol with 0.5% of water to analyze AFE and ethanol with 7% of water to analyze HFE. They did not find significant differences between found concentrations by matrix matching in ICP-OES and isotope dilution in ICP-MS. Additional studies have tried to minimize non spectral interferences in the analysis of metals in bioethanol and fuel ethanol through matrix matching.[38,180,181,184,190] Unfortunately, this method is time consuming and inaccurate in many cases because normally the matrix of the sample is very complex and/or unknown.

Internal standardization can be applied in order to carry out an accurate and precise analysis of ethanol and ethanol fuel.[184,190] This methodology shows, as the most important concern the correct selection of the best internal standard. Tormen *et al*.[186] evaluated ytrium, rhodium and iridium as internal standards to analyze 19 elements by ICP-MS. External calibration was taken as reference. The authors concluded that ytrium or even rhodium could be satisfactorily employed as an IS in the routine analysis of fuel ethanol. However, provided that the samples were diluted the found concentrations for V, Ni, Ga, Sr, Cd, Sn and Tl were below the limit of quantification.[186]

Isotopic dilution, in turn, has been applied in order to minimize or remove non-spectral interferences in ICP-MS with good results.[38,181,186] This method shows several advantages against internal standard calibration because it is very simple, fast and clean.[181]

Alternative sample introduction systems

The spray chamber can be cooled in order to minimize the mass of organic material reaching the plasma.[172,173] Thus, for instance, a cyclonic spray chamber was operated at 10ºC with the aim of determining Cu, P and S in ethanol through ICP-OES with recoveries between 93.5 and 107.3%.[172] An alternative approach is a spray chamber cooled by a Peltier effect based system making it possible to introduce pure ethanol into the plasma.

Desolvation systems are based on a previous aerosol heating step followed by either a membrane or a condenser. The first stage promotes the efficient solvent evaporation from the aerosol whereas the second one removes the generated vapor. This device is also appropriate to overcome matrix effects. Alcohols have been analyzed through ICP-OES with membrane desolvator[193] or cryogenic desolvation.[194] Rocha *et al.*[184] reported a method allowing the determination of Cu and Fe in AFE and HFE through ICP-OES by direct sample introduction using an ultrasonic nebulizer and membrane desolvator (USN-MD-ICP-OES) and they obtained LODs similar to those previously reported in ICP-MS.[38,181,186] Saint´Pierre *et al.*[38] employed a flow injection system coupled to an ultrasonic nebulizer and desolvator to carry out the analysis of AFE and HFE in ICP-MS. The obtained LODs for Ag, Cd, Co, Cu, Fe, Mn, Ni and Pb were higher than those found by ETV-ICP-MS.[38,180]

Additional systems employed for bioethanol and ethanol fuel samples analysis include low sample consumption systems. A microconcentric nebulizer (MCN) was used by Tormen *et al.*[186] to carry out the determination of Cu, Cd, Ni, Pb, Tl and Sn in fuel ethanol through ICP-MS. Compared with conventional nebulizers, MCN showed lower limits of detection and better precision even at lower sample consumption rates. This was due to the finer primary aerosols and higher analyte transport efficiencies as compared to conventional nebulization systems.[195] External calibration and internal standardization were applied and the results were in concordance with those found with isotopic dilution.[186] With this device it was possible to introduce in the plasma 70% ethanol solutions. For higher ethanol concentrations carbon deposits appeared in the ICP-MS interface cones.[186]

Electrothermal vaporization (ETV) is a good approach to remove non spectral interferences when ethanol and fuel ethanol are analyzed.[180,181,192] Nonetheless, few authors have reported methods to carry out the determination of some elements in this kind of samples through ETV coupled to ICP-MS.[180,181] Saint´Pierre *et al.*[181] reported a method to determine trace metals in ethanol fuel by Isotopic Dilution ETV- ICP/MS. In this study Ag, Cd, Cu, Pb and Tl were determined in fuel alcohol with LOD of 0.02, 0.08, 0.1, 0.05, 0.001 µg L^{-1}, respectively (Table 6~~Table 6~~). For Cd, Pb and Tl that evaporated at lower temperatures, the use of Pd aqueous solution as chemical modifier was necessary. However, in the Ag and Cu determination it was not necessary to use chemical modifiers because these elements showed lower volatilities than Cd, Pb and Tl.[181] In another study, the determination of Ag, As, Cd, Cu, Co, Fe, Mn, Ni, Sb, Sn, and Tl in ethanol fuel was successfully done through ETV-ICP-MS using external calibration with ethanolic solutions and Pd as chemical modifier.[180] Recoveries for all elements were between 80 and 120% without modifier and from 60 to 140% with palladium.

Spectral interferences

Spectral interferences in ICP techniques when organic samples (*e.g.* ethanol) are introduced have been extensively described by several authors.[119,196] In ICP-OES these interferences are related with peak overlapping.[197] Polyatomic interferences occur in ICP-MS when ethanol is injected into the plasma. For example, $^{12}C_2^+$, $^{12}C^{14}N^+$, $^{13}C^{14}N^+$, $^{12}C^{16}O^+$, $^{13}C^{16}O^+$, $^{12}C^{17}O^+$, $^{40}Ar^{12}C^+$, $^{40}Ar^{13}C^+$ may interfere on $^{24}Mg^+$, $^{26}Mg^+$, $^{27}Al^+$, $^{28}Si^+$, $^{29}Si^+$, $^{52}Cr^+$ and $^{53}Cr^+$ determination, respectively.[198] Recently, Neves *et al.*[190] verified that flow-rates below 112.5 mL min^{-1} were insufficient to remove the formed carbon compounds when ethanol concentration was higher than 80%. On the other hand, an excess of oxygen in the plasma could cause the formation of metal oxide polyatomic species.[110]

Additional possibilities to remove spectral interferences due to polyatomic species in ICP-MS when ethanol and fuel ethanol are analyzed are the use of a dynamic collision cell (DCC), dynamic reaction cell (DRC) or collision-reaction interface (CRI). Kishi *et al.*[199] reported a reduction of carbon-based interferences in alcohols using a DRC with pure ammonia as a reaction gas. Neves *et al.*[190] evaluated the use of He or H_2 as collision and reaction gases in a CRI system and they observed that the introduction of either two gases through the sampling cone was inefficient whereas opposite effect was observed when H_2 was introduced through the skimmer cone. The signal at m/z = 56 due to $^{40}Ar^{16}O^+$ was around 12-fold lower when 60 mL min^{-1} H_2 or He were introduced through the skimmer cone in comparison with the signals without insertion of these gases. A similar behavior was observed for $^{24}Mg^+$ ($^{12}C_2^+$), $^{28}Si^+$ ($^{12}C^{16}O^+$) and $^{52}Cr^+$ ($^{40}Ar^{12}C^+$) showing the capability of this device to reduce isobaric interferences when ethanol was analyzed. In the same study it was verified that reaction mode using H_2 was more effective than collision mode with He.

4.3. Analysis by other techniques

Although ICP based techniques have been the most widely used to carry out the determination of metals and metalloids in ethanol fuel, alternative methods have been explored such as ETAAS,[175,200–205] FAAS,[176,179,185,206–209] voltammetry,[183,210,211] ionic chromatography (IC)[178] or microwave plasma optical emission spectrometry (MIP-OES).[177]

Several modifiers have been used to carry out the determination of metals in bioethanol and ethanol fuel by ETAAS. The most used one corresponds to a mixture of $Pd(NO_3)_2$ and $Mg(NO_3)_2$[200–202] although permanent modifiers as W-Rh mixture[201], Ru-Zr[203], Ir-Rh[204] or W-Ir (co-injected) have also been evaluated.[175] De Oliveira *et al.*[200] carried out a comparative study of chemical modifiers employed to determine metals in ethanol fuel. Three possibilities were studied for six elements, $Pd(NO_3)_2$ + $Mg(NO_3)_2$, W/Rh and W + co-injection of $Pd(NO_3)_2$ + $Mg(NO_3)_2$. The last one was the modifier providing the best recoveries.

De Oliveira *et al.*[201,202] developed two methods to carry out the determination of metals in fuel ethanol through ETAAS. In the first method they determined Al, As, Cu, Fe, Mn and Ni in ethanol fuel using a transversely heated graphite atomizer (THGA) and a $Pb(NO_3)_2$ and $Mg(NO_3)_2$ mixed modifier. The recoveries obtained went from 73 to 116% and the RSD for all elements was lower than 6%.[202] In the second method they used W-Rh permanent modifier together with $Pd(NO_3)_2$ + $Mg(NO_3)_2$. The values of RSD and LOD (Table 6~~Table 6~~) were similar to those achieved without permanent modifier and recoveries were between 81 and 109%.[201]

Saint Pierre *et al.*[203] evaluated several modifiers in order to perform the direct determination of As, Cu, Fe, Pb, Sb and Sn in ethanol fuel by ETAAS. Finally, they proposed to determine Cu and Fe without chemical modifier whereas Ru was selected as modifier to determine As, Sb, Sn and Pb. In the case of Pb, $NH_4H_2PO_4$ could be employed as an alternative modifier. Recoveries were included within the 89.3 to 103.8% range.[203] Giacomelli *et al*.[204] studied the use of Ir together with Rh as a permanent modifier to determine As, Cd and Pb in pure ethanol by ETAAS. In this case, the obtained recoveries were between 94 and 96.7%. Saint´Pierre *et al*.[205] reported a method to determine Cd and Pb in fuel ethanol by ETAAS. The standards were prepared in ethanol and the recoveries ranged from 90 to 120%.

Recently, Santos *et al*.[175] have developed a method for simultaneous determination of Cu and Pb in ethanol fuel by ETAAS using a transversely heated graphite atomizer with W as permanent modifier and co-injecton of Ir. Recovery was between 93 and 103 % for Cu and from 96 to 110% for Pb while RSD was below 1% in all the cases.

Because FAAS provides higher limits of detection than techniques described previously (ICP-OES, ICP-MS and ETAAS), the use of this technique to perform ethanol fuel analysis involves a previous preconcentration stage.[176,179,185,207–209] Thus Alves *et al*.[185] developed a method to determine Cd in ethanol fuel through FAAS using *Moringa oleifera* seeds as a on-line biosorbent to carry out the samples preconcentration. The recoveries for three samples were from 97.5 to 100% and LOD was 5.50 μg L^{-1}. The same authors had developed a similar work using vermicompost as the adsorbent material and acceptable results in terms of precision and accuracy were obtained.[209] Several authors have reported on the determination of different metals through FAAS using modified silica gel as a preconcentration media.[176,179,206–208] De Melo *et al.*[207] employed a column with 5-amino-1,3,4-thiadiazole-2-thiol modified silica gel to preconcentrate Cd(II), Co(II), Fe(III), Ni(II), Pb(II) and Zn(II). The recoveries obtained were between 98 and 99%. A column with 2,5-dimercapto-1,3,4-thiadiazole modified silica gel was used to determine Cu(II), Zn(II), Cd(II), Ni(II), Pb(II), Co(II) and Fe(III) in ethanol fuel. Recoveries close to 100% were found for binary mixtures whereas they were lower for mixtures of all elements (20-30% for Cd).[208] Additional adsorbing media have been described such as 2-aminothiazole[179] modified silica gel or *N*-Acyl-*N*´-Benzoylthiourea modified silica gel.[206] Recently, Vieira *et al.*[176] have used 2,2´-dipyridylamine bonded silica as a preconcentration system to determine Fe(III), Cr(III), Cu(II), Co(II), Pb(II), Ni(II) and Zn(II) in fuel ethanol through FAAS. The recovery obtained for all the analytes was close to 100% and accuracy was good with RSD for all elements lower than 3%. The concentrations found and LODs for all methods proposed[176,179,185,207,208] are shown in

Table 6~~Table 6~~.

Donati *et al.*[177] have developed a method to determine Cr, Ni, Pb and V in ethanol fuel through MIP-OES. The samples have been diluted in an aqueous nitric acid medium. The method supplied good precision and accuracy, the recoveries being included in the 92 to 108% range.

Voltammetry can also be useful to determine metals in ethanol fuel and water-ethanol mixtures. A method to determine Cd in alcohol-water mixtures using an ion-selective electrode was developed by Motonaga *et al.*[210] It was found that cadmium ion-selective electrodes could be used to determine Cd ions in an alcohol-water mixture. Nevertheless, the response time became longer and the dynamic range was narrower as the ethanol content went up. Kamenev *et al.*[211] carried out the determination of Pb(II) in water-alcohol mixtures by Stripping Voltammetry with a modified carbon-Glass-Ceramic electrode. The procedure was based on electrochemical and chemical modification of the surface and provided reproducible results. Another method was based on anodic stripping voltammetry (ASV)[183] with the aim of determine Cu and Pb simultaneously. Two different procedures were applied: the first one was the direct quantification of metals in alcohol-water mixtures whereas the second one involved the evaporation of organic solvent and re-suspension of ions in water + electrolyte. The results obtained with two methods were in good agreement.

A high-performance chelation ionic chromatography method was used to quantify Fe^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} in fuel ethanol through post-column reaction with 4-(2-pyridylazo)resorcinol and spectrophotometric detection at 510 nm.[178]

4.2.3. Speciation

Only two studies have been developed to carry out the speciation of metals in ethanol fuel.[178,212] In both cases, high-performance chelation ion chromatography has been employed to separate Fe^{2+}, Fe^{3+} and additional cations. The chromatographic system is based on a silica column functionalized with iminodiacetic acid (IDA) groups and photometric detection at 510 nm by post-column reaction with 4-(2-pyridylazo)resorcinol (PAR). In the first study, the eluent was a solution containing 2.5 mmol L^{-1} of DPA and 5 mmol L^{-1} of HCl in a mixture 60% methanol : 40% water.[178] In the second one, a solution containing 2 mmol L^{-1} of chelidamic acid (CDA), 3 mmol L^{-1} of triethylamine (TEA) and 12 mmol L^{-1} of HCl in a mixture 50% methanol : 50% water was employed as mobile phase.[212] The recoveries for both iron species went from 90 to 103%.[178,212]

Table 6. Summary of the limits of detection and found concentrations obtained in fuel ethanol samples by several authors.*

Element	**Technique**	**Conditions**	**LOD (µg L^{-1})**	**Found concentration (µg L^{-1}) Range (min-max)**	**Ref.**
Ag	ETV-ICP-MS	ID	0.02	< 0.02 – 0.079	[181]

		EC	0.02	< 0.02 – 0.072	
	ETV-ICP-MS	EC (Pd as modifier)	0.013	0.041 – 0.102	180
	ETV-ICP-MS	EC	0.015	< 0.015 – 0.072	
	FI-USN-ICP-MS	EC (W)	0.1	n.d.	38
		EC (MM)	0.07	n.d.	
		ID	0.02	n.d.	
	ICP-OES	EC Cooled spray chamber Ag 328.028	0.47	n.d.	173
Al	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.20	33 – 411	190
	ETAAS	EC (Ethanol 1:1) THGA with $Pd(NO_3)_2$ + $Mg(NO_3)_2$	1.2	n.a	202
	ETAAS	EC (Ethanol 1:1) W-Rh permanent modifier and $Pd(NO_3)_2$ + $Mg(NO_3)_2$	1.9	n.a	201

	ICP-OES	EC Cooled spray chamber Al 167.020	0.15	n.a	173
	ICP-OES	EC Cooled spray chamber Al 396.152	2.68	n.a	173
As	ETV-ICP-MS	EC (Pd as modifier)	0.02	0.23 – 2.84	180
	ETV-ICP-MS	EC	0.04	< 0.04 – 2.03	
	ETAAS	EC (Ethanol 1:1) THGA with $Pd(NO_3)_2$ + Mg $(NO_3)_2$	2.5	n.d.	202
	ETAAS	EC (Ethanol 1:1) W-Rh permanent modifier and $Pd(NO_3)_2$ + $Mg(NO_3)_2$	2.9	n.d.	201
	ETAAS	EC Ru as modifier	0.7	n.d.	203
	ETAAS	EC	2.0	< 2.0 – 2.7	204

		Ir + Rh as modifier			
	ICP-OES	EC Cooled spray chamber As 189.042	2.22	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.01 – 0.03$^{\#}$	1.13 – 3.62$^{\$}$	186
B	ICP-OES	EC Cooled spray chamber B 249.773	1.42	n.d.	173
Ba	ICP-OES	EC Cooled spray chamber Ba 455.403	0.04	n.d.	173
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.11	< 0.11	190
Be	ICP-OES	EC Cooled spray chamber Be 313.042	0.21	n.d.	173
Bi	MCN-ICP-MS	EC and Y, Ir and Rh	0.02$^{\#}$	< 0.02 – 0.17$^{\$}$	186

		as IS			
Ca	ICP-OES	EC Cooled spray chamber Ca 317.933	1.56	n.d.	173
Cd	ETV-ICP-MS	ID (Pd as modifier)	0.08	< 0.08 – 0.53	181
		EC (Pd as modifier)	0.07	< 0.07 – 0.54	
	ETV-ICP-MS	EC (Pd as modifier)	0.07	< 0.07 – 1.15	180
	ETV-ICP-MS	EC	0.13	< 0.13 – 1.05	
	FI-USN-ICP-MS	EC (W)	0.2	n.d.	38
		EC (MM)	0.03	n.d.	
		ID	0.02	n.d.	
	FAAS	EC Using *Moringa oleifera* seeds as a biosorbent	5.50	n.d.	185
	ETAAS	EC Ir + Rh as modifier	0.05	< 0.05 – 3.0	204
	ETAAS	EC with pure ethanol	0.1	< 0.1 – 0.83	205

		Filter-ETAAS			
	ICP-OES	EC Cooled spray chamber Cd 228.802	0.17	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	$0.03 – 0.05^{\#}$	$< 0.05^{\$}$	186
Co	ETV-ICP-MS	EC	0.002	0.011 – 0.094	180
	FI-USN-ICP-MS	EC (W)	0.04	n.d.	38
		EC (MM)	0.5	n.d.	
	FAAS	Preconcentration with 2,2´-dipyridylamine bonded silica	0.44	n.d.	176
	ICP-OES	EC Cooled spray chamber Co 228.616	0.32	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	$0.03^{\#}$	$< 0.1^{\$}$	186
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.05	5.6 – 26.1	190

Cr	FAAS	Preconcentration with 2,2´-dipyridylamine bonded silica	0.33	n.d.	176
	MIP-OES	EC ethanol 10%	9	< 9	177
	ICP-OES	EC cooled spray chamber Cr 267.716	0.35	n.d.	173
	USN-CD-ICP-OES	EC	0.8	n.d.	194
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.18	12.3 – 77.2	190
Cu	ETV-ICP-MS	ID	0.1	1.96 – 14.44	181
		EC	0.2	1.80 – 14.98	
	ETV-ICP-MS	EC	0.22	1.80 – 14.98	180
	ETAAS	EC	n.a.	2.15 – 13.93	
	FAAS	5-amino-1,3,4-thiadiazole-2-thiol modified silica gel preconcentrated	n.a.	52-78	207
	FAAS	Preconcentrated by evaporation	n.a.	49-76	207

	FAAS	Preconcentrated by 2,5-dimercapto-1,3,4-thiadiazole	n.a.	11-190* *5000 for a sample in a copper distillation column	208
	FI-USN-ICP-MS	EC (W)	0.4	n.d.	38
		EC (MM)	0.8	n.d.	
		ID	0.2	n.d.	
	FAAS	Preconcentrated with 2-aminothiazole modified silica gel	1.7	5.4 – 7.3	179
	FAAS	Preconcentrated with 2-aminothiazole modified silica gel	n.a.	5.4 – 7.3	179
	FAAS	Preconcentration with 2,2´-dipyridylamine bonded silica	0.40	51 – 66	176
	FAAS	Preconcentrated by evaporation	n.a.	49 – 57	176
	ETAAS	EC (Ethanol 1:1) THGA with	0.22	n.d.	202

		$Pd(NO_3)_2$ + Mg $(NO_3)_2$			
	ETAAS	EC (Ethanol 1:1) W-Rh permanent modifier and $Pd(NO_3)_2$ + $Mg(NO_3)_2$	0.57	n.d.	201
	ETAAS	EC Without modifier	0.6	2.15 – 13.93	203
	GFASS	W permanent modifier + co-injection of Ir	0.086	8.0 – 47	175
	FAAS	EC Preconcentration with *N*-Acyl-*N*-Benzoylthiourea modified silica gel	n.a.	6.9 – 7.2	206
	ASV	IS Evaporation of ethanol and redisolution in aqueous media	0.120	13.3 – 20.1	183
	HPCIC	EC (Cu^{2+})	7.4	n.d.	178

	ICP-OES	EC Colled spray chamber Cu 324.754 nm	1.5	n.d.	172
	ICP-OES	EC cooled spray chamber Cu 324.754	0.28	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.09 – $0.2^{\#}$	3.1 – $24.1^{\$}$	186
	USN-MD-ICP-OES	EC(MM) in AFE	0.10	< 0.10 – 2.20	184
	USN-MD-ICP-OES	EC(MM) in HFE	0.23	2.58 – 2.75	184
	USN-CD-ICP-OES	EC	0.3	n.d.	194
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.33	23 – 205	190
Fe	ETV-ICP-MS	EC	0.72	6.55 – 42.99	180
	ETAAS	EC	n.a.	6.88 – 29.43	
	FAAS	5-amino-1,3,4-thiadiazole-2-thiol modified silica gel	n.a.	12 – 23	207

		preconcentrated			
	FAAS	Preconcentrated by evaporation	n.a.	11 – 21	207
	FAAS	Preconcentrated by 2,5-dimercapto-1,3,4-thiadiazole	n.a.	n.d. – 7	208
	FI-USN-ICP-MS	EC (W)	27	n.d.	38
		EC (MM)	10	n.d.	
	FAAS	Preconcentration with 2,2´-dipyridylamine bonded silica	0.28	10 – 25	176
	FAAS	Preconcentrated by evaporation	n.a.	11 – 21	176
	ETAAS	EC (Ethanol 1:1) THGA with $Pd(NO_3)_2$ + Mg $(NO_3)_2$	1.6	n.d.	202
	ETAAS	EC (Ethanol 1:1) W-Rh permanent modifier and $Pd(NO_3)_2$ + $Mg(NO_3)_2$	1.3	n.d.	201

	ETAAS	EC Without modifier	1.4	6.88 – 29.43	203
	HPCIC	EC (Fe^{3+})	8.9	n.d.	178
	ICP-OES	EC cooled spray chamber Fe 259.940	0.52	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.7 – 4$^{\#}$	< 4 - 18$^{\$}$	186
	USN-MD-ICP-OES	EC(MM) in AFE	0.20	< 0.20 -13.95	184
	USN-MD-ICP-OES	EC(MM) in HFE	0.50	5.34 – 5.80	184
	ID-ICP-MS	ID in AFE	n.a.	14.20	184
	ID-ICP-MS	ID in HFE	n.a.	5.30 – 5.75	184
	USN-CD-ICP-OES	EC	0.6	n.d.	194
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.10	6- 124	190
Ga	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.06 – 0.2$^{\#}$	< 0.2$^{\$}$	186
Hg	ICP-OES	EC cooled spray	1.80	n.d.	173

		chamber Hg 194.163			
K	ICP-OES	EC cooled spray chamber K 766.490	29.67	n.d.	173
Li	ICP-OES	EC cooled spray chamber Li 670.784	0.65	n.d.	173
Mg	ICP-OES	EC cooled spray chamber Mg 279.806	4.01	n.d.	173
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.24	17 – 204	190
Mn	ETV-ICP-MS	EC	0.025	0.884 – 1.306	180
	FI-USN-ICP-MS	EC (W)	0.7	n.d.	38
		EC (MM)	0.8	n.d.	
	ETAAS	EC (Ethanol 1:1) THGA with $Pd(NO_3)_2$ + Mg	0.20	n.d.	202

		$(NO_3)_2$			
	ETAAS	EC (Ethanol 1:1) W-Rh permanent modifier and $Pd(NO_3)_2$ + $Mg(NO_3)_2$	0.40	n.d.	201
	ICP-OES	EC cooled spray chamber Mn 257.610	0.13	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.02 – 0.4#	0.77 – 1.25$	186
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.02	1.7 – 15.4	190
Mo	ICP-OES	EC cooled spray chamber Mo 202.030	0.45	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.03#	< 0.03 – 0.46$	186
	CRI-ICP-MS	IS (Y) CRI (H_2 through	0.05	< 0.05	190

		skimmer)			
Na	ICP-OES	EC cooled spray chamber Na 589.592	4.96	n.d.	173
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.80	54 – 184	190
Ni	ETV-ICP-MS	EC	0.026	0.096 – 0.477	180
	FAAS	5-amino-1,3,4-thiadiazole-2-thiol modified silica gel preconcentrated	n.a.	8 – 14	207
	FAAS	Preconcentrated by evaporation	n.a.	10 – 13	207
	FAAS	Preconcentrated by 2,5-dimercapto-1,3,4-thiadiazole	n.a.	5 – 45	208
	FI-USN-ICP-MS	EC (W)	0.4	n.d.	38
		EC (MM)	2.5	n.d.	
	FAAS	Preconcentrated with 2-aminothiazole	2.3	4.4 – 5.6	179

		modified silica gel			
	ETAAS	EC	n.a.	4.1 – 6.1	179
	FAAS	Preconcentration with 2,2´-dipyridylamine bonded silica	0.51	9 – 15	176
	FAAS	Preconcentrated by evaporation	n.a.	10 – 13	176
	ETAAS	EC (Ethanol 1:1) THGA with $Pd(NO_3)_2$ + Mg $(NO_3)_2$	1.1	n.d.	202
	ETAAS	EC (Ethanol 1:1) W-Rh permanent modifier and $Pd(NO_3)_2$ + $Mg(NO_3)_2$	1.3	n.d.	201
	MIP-OES	EC ethanol 10%	300	< 300	177
	ICP-OES	EC cooled spray chamber Ni 221.647	0.30	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh	$0.1 – 0.5^{\#}$	$< 0.5^{\$}$	186

		as IS			
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.17	14 – 73	190
P	ICP-OES	EC Colled sprat chamber P 177.495 nm	11	n.d.	172
	ICP-OES	EC cooled spray chamber P 177.440	4.92	n.d.	173
	ICP-OES	EC cooled spray chamber P 178.229	4.32	n.d.	173
	ICP-OES	EC cooled spray chamber P 213.618	2.63	n.d.	173
Pb	ETV-ICP-MS	ID (Pd as modifier)	0.05	0.62 – 1.58	181
		EC	0.02	0.51 – 1.51	

		(Pd as modifier)			
	ETV-ICP-MS	EC (Pd as modifier)	0.02	0.57 – 1.50	180
	ETV-ICP-MS	EC	0.03	0.39 – 1.51	
	FI-USN-ICP-MS	EC (W)	0.2	n.d.	38
		EC (MM)	0.1	n.d.	
		ID	0.04	n.d.	
	FAAS	Preconcentration with 2,2´-dipyridylamine bonded silica	0.55	n.d.	176
	ETAAS	EC Ru as modifier	0.7	n.d.	203
	ETAAS	EC $NH_4H_2PO_4$ as modifier	0.7	n.d.	203
	ETAAS	EC Ir + Rh as modifier	1.1	< 1.1 – 6.4	204
	ETAAS	EC with pure ethanol Filter-ETAAS	0.3	< 0.3 – 1.16	205
	GFASS	W permanent modifier + co-	2.47	< 2.47	175

		injection of Ir			
	ASV	IS Evaporation of ethanol and redisolution in aqueous media	0.235	< 0.235 – 1.43	183
	MIP-OES	EC ethanol 10%	500	< 500	177
	ICP-OES	EC cooled spray chamber Pb 220.353	1.68	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.03#	< 0.03 – 1.08$	186
	USN-CD-ICP-OES	EC	5	n.d.	194
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.01	5.6 – 38	190
Rb	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.03#	< 0.1$	186
S	ICP-OES	EC Colled sprat chamber S 180.731	21	n.d.	172

	ICP-OES	EC cooled spray chamber S 180.676	5.13	n.d.	173
Sb	ETAAS	EC Ru as modifier	1.8	n.d.	203
	ICP-OES	EC cooled spray chamber Sb 206.833	2.30	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.02#	n.d.	186
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	0.11	< 0.11	190
Se	ICP-OES	EC cooled spray chamber Se 196.026	39.63	n.d.	173
	MCN-ICP-MS	IS (Y)	0.6	1.8 – 3.3	186
Si	ICP-OES	EC cooled spray chamber	1.84	n.d.	173

		Si 251.611			
	CRI-ICP-MS	IS (Y) CRI (H_2 through skimmer)	14	< 14	190
Sn	ETV-ICP-MS	EC (Pd as modifier)	0.010	< 0.010 – 0.062	180
	ETV-ICP-MS	EC	0.007	< 0.007 – 0.067	
	ETAAS	EC Ru as modifier	3.8	n.d.	203
	ICP-OES	EC cooled spray chamber Sn 189.989	2.83	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	$0.09^{\#}$	$< 0.09^{\$}$	186
Sr	ICP-OES	EC cooled spray chamber Sr 407.771	0.01	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	$0.01 – 0.03^{\#}$	$< 0.03^{\$}$	186
Ti	ICP-OES	EC cooled spray	0.13	n.d.	173

		chamber Ti 337.280			
Tl	ETV-ICP-MS	ID (Pd as modifier)	0.001	< 0.001 – 0.0047	181
		EC (Pd as modifier)	0.0008	< 0.0008 – 0.0045	
	ETV-ICP-MS	EC (Pd as modifier)	0.0008	< 0.0008 – 0.0045	180
	ETV-ICP-MS	EC	0.0009	< 0.0009 – 0.0045	
	ICP-OES	EC cooled spray chamber Tl 190.864	2.66	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.01$^{\#}$	< 0.01$^{\$}$	186
V	MIP-OES	EC ethanol 10%	4	< 4	177
	ICP-OES	EC cooled spray chamber V 292.402	3.59	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.06 – 0.5$^{\#}$	< 0.5$^{\$}$	186
	CRI-ICP-MS	IS (Y)	0.41	< 0.4	190

		CRI (H_2 through skimmer)			
Zn	FAAS	5-amino-1,3,4-thiadiazole-2-thiol modified silica gel preconcentrated	n.a.	6 – 8	207
	FAAS	Preconcentrated by evaporation	n.a.	8 – 11	207
	FAAS	Preconcentrated by 2,5-dimercapto-1,3,4-thiadiazole	n.a.	3 – 4.5	208
	FAAS	Preconcentrated with 2-aminothiazole modified silica gel	0.34	6.3 – 8.3	179
	ETAAS	EC	n.a.	7.1 – 8.1	179
	FAAS	Preconcentration with 2,2´-dipyridylamine bonded silica	0.58	6 – 10	176
	FAAS	Preconcentrated by evaporation	n.a.	8 – 11	176
	FAAS	EC	n.a.	1.0 – 2.4	206

		Preconcentration with *N*-Acyl-*N*-Benzoylthiourea modified silica gel			
	HPCIC	EC (Zn^{2+})	2.0	n.d.	178
	ICP-OES	EC cooled spray chamber Zn 206.200	0.53	n.d.	173
	ICP-OES	EC cooled spray chamber Zn 213.856	0.60	n.d.	173
	MCN-ICP-MS	EC and Y, Ir and Rh as IS	0.4 – 0.6$^{\#}$	14.4 – 36.1$^{\$}$	186
	USN-CD-ICP-OES	EC	0.3	n.d.	194
	CRI-ICP-MS	IS (Y) CRI (H$_2$ through skimmer)	0.26	17 – 400	190

*ID: Isotopic Dilution; EC: External Calibration; EC (W): External Calibration with water; EC (MM): External calibration with matrix matching.

n.d.: non determined in real samples; n.a.: not available data.

[#] These ranges correspond to minimum and maximum values of LOD obtained with the four types of calibration employed by the authors (External calibration and internal standardization using Ir, Rh and Y).

[$] Concentration values have been obtained employing Y as internal standard.

4.4 Comparison among techniques.

As it has been previously discussed, several techniques have been employed to quantify metals in bioethanol and fuel ethanol samples. Generally speaking the elemental concentration in this kind of samples is very low (Table 6~~Table 6~~) and, hence, it is necessary to select a sensitive enough technique. For this reason ICP-OES and ICP-MS are widely used[10,14,20,22–24,30,37,38,41,172,173,180,181,184,186,189–195,199] because it is possible to carry out the sample analysis without any pre-concentration step. Unfortunately, these techniques are quite sensitive to spectral as well as non-spectral interferences that could be circumvented by applying dedicated approaches.[38,172,173,180,181,192–195,199] Another technique that has been frequently used to determine metals in fuel ethanol is ETAAS.[175,200–205] Meanwhile, techniques such as voltammetry[183,210,211], chromatographic techniques[178] or MIP-OES[177] are less frequently employed.

Figure 5~~Figure 6~~ shows the percentage of studies carried out with each technique for all the elements studied in the literature. This data have been obtained from data collected in Table 6~~Table 6~~. The data of Y-axis have been obtained according to Equation 2.

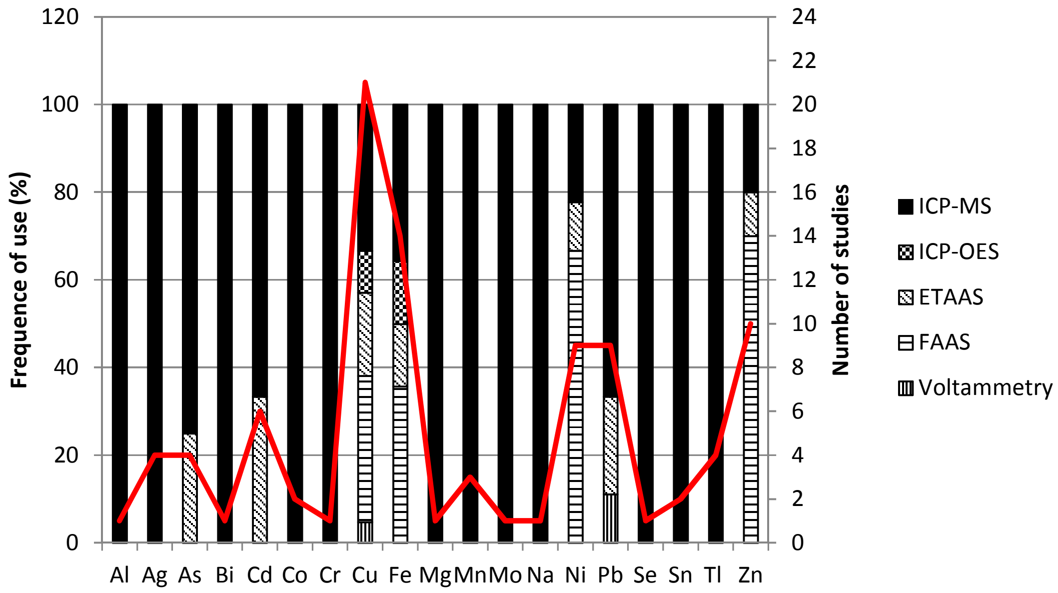

Figure 5~~6~~. Techniques employed for the determination of several metals in biodiesel samples (bars) and number of studies dealing with the determination of each one of the elements (red line).

As Figure 5~~Figure 6~~ suggests, ICP-MS is the most widely employed technique. ICP-OES, in turn, has been used for the determination of 7 elements present at concentrations of around a few µg L^{-1}. However, because ICP-based techniques are very sensitive to organic solvents, ETAAS has been used as a good alternative. On the other hand, FAAS and some chromatographic techniques have been applied to the determination of major elements (Figure 5~~Figure 6~~ Figure 6) in bioethanol and fuel ethanol.

4.5. Standards for the analysis of bioethanol

Table 7 gathers the existing Standards for the elemental determination in ethanol employed for fuel applications. It is interesting to notice that in some instances, methods such as colorimetry or potentiometry are recommended. This situation does not correspond to that presented in Figure 5~~Figure 6~~ issued from the research articles included in the present review. As regards ICP-OES and ICP-MS these techniques are seldom considered. A similar comment can be made regarding atomic absorption techniques.

Table 7. Standards for the elemental determination in ethanol employed for fuel applications.

Standard reference	**Standard title**	**Determined elements**	**Analytical technique**	**Year**
EN 15485	Ethanol as a blending component for petrol - Determination of sulfur content - Wavelength dispersive X-ray fluorescence spectrometric method	S	WDXRF	2007
EN 15486	Ethanol as a blending component for petrol - Determination of sulfur content - Ultraviolet fluorescence method	S	UVF	2007
EN 15487	Ethanol as a blending component for petrol - Determination of phosphorus content - Ammonium molybdate spectrometric method	P	Colorimetry	2007

EN 15488	Ethanol as a blending component for petrol - Determination of copper content - Graphite furnace atomic absorption spectrometric method	Cu	ETAAS	2007
EN 15492	Ethanol as a blending component for petrol - Determination of inorganic chloride and sulfate content - Ion chromatographic method	Cl, S	Ionic Chromatography	2012
EN 15837	Ethanol as a blending component for petrol - Determination of phosphorus, copper and sulfur content - Direct method by inductively coupled plasma optical emission spectrometry (ICP OES)	P, Cu, S	ICP-OES	2010
ASTM D7319	Standard Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion	Cl, S	Ionic Chromatography	2013

	Chromatography			
ASTM D7039	Standard Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry	S	MWDXRF	2013
ASTM D7328	Standard Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection	Cl, S	Ionic Chromatography	2013
ASTM D7318	Standard Test Method for Existent Inorganic Sulfate in Ethanol by Potentiometric Titration	S	Potentiometry	2013
ASTM D5798	Standard Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark-Ignition Engines	Specifications*		2014

ASTM D4806	Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel	Specifications*		2014
*These standards refer to :				
ASTM D5453 (S by UVF)		S	UVF	2012
ASTM D2622 (S by XRF)		S	WDXRF	2010
ASTM D5059 (Pb by XRF)		Pb	WDXRF	2014
ASTM D3231 (P by colorimetry)		P	Colorimetry	2013

In Brazil, where bioethanol and ethanol fuel are widely used, the quality of fuel ethanol is carefully regulated by the National Agency of Petroleum (ANP).[178,179,183,184] However, only a standard for sulfur and copper (D4806-07a;[172] D3237[177]) and another for iron (D1688-07[184]) have been establish by ASTM. Besides, in 2009 an european standard for Cu, P and S was published.[188] The most widely employed techniques to quantify metals in biofuel products are ICP-OES, ICP-MS, ETAAS and FAAS.

5. Conclusions

Summarizing the results obtained in the literature, Figure 6~~Figure 7~~ shows the elements found in biofuel samples. Data from Table 4~~Table 3~~ and Table 6~~Table 6~~ have been employed. The considered data correspond to ‘pure’ biodiesel and fuel ethanol samples. It is important to note that metal concentration in blend biodiesel has not been taken into account. Since, there are no clear data regarding the metal concentration in only bioethanol, the results corresponding to fuel ethanol are included in Figure 6~~Figure 7~~. A code indicating the metal content is also applied in order to distinguish major elements from trace elements.

The results concerning biodiesel characterization are more abundant than those corresponding to bioethanol analysis. Thus, in the first case, official directives have been developed so as to assure the quality of the employed fuel. This is in clear constrast with the situation found when bioethanol samples are considered. In that case, the studies provide information about the concentration of metals in the blend corresponding to bioethanol and gasolie (fuel ethanol). As a result, it is difficult to discern among the different sources of metallic species. It is also interesting to notice that there are no data regarding organometallic speciation in this kind of products. Additional data regarding isotopic analysis are also scarce. This information would provide a better insight in the toxic potential of the different fuels. Furthermore, they would also give information about the geographical origin as well as the raw materials employed for production.

According to the information reviewed in the present work, it is obvious that additional work is required based on the development of more sensitive methods and less prone to interferences than the existing ones. In this sense, the work related with new ICP liquid sample introduction systems able to mitigate non spectral interferences while increasing the sensitivity is highly promising. Likewise, the use of robust ICP-MS equipped with collision and/or reaction cells to overcome spectral interferences should be encouraged. Standards must adapt to the new developments in this field and propose ICP analytical tools because they can provide a multielemental information in a quick fashion and they afford suitable analytical figures of merit. Simple, fast and chip pre-treatment methods for biodiesel and bioethanol analysis aimed at pre-concentrating the sample while removing the matrix are extremely useful and more effort is needed in this field.

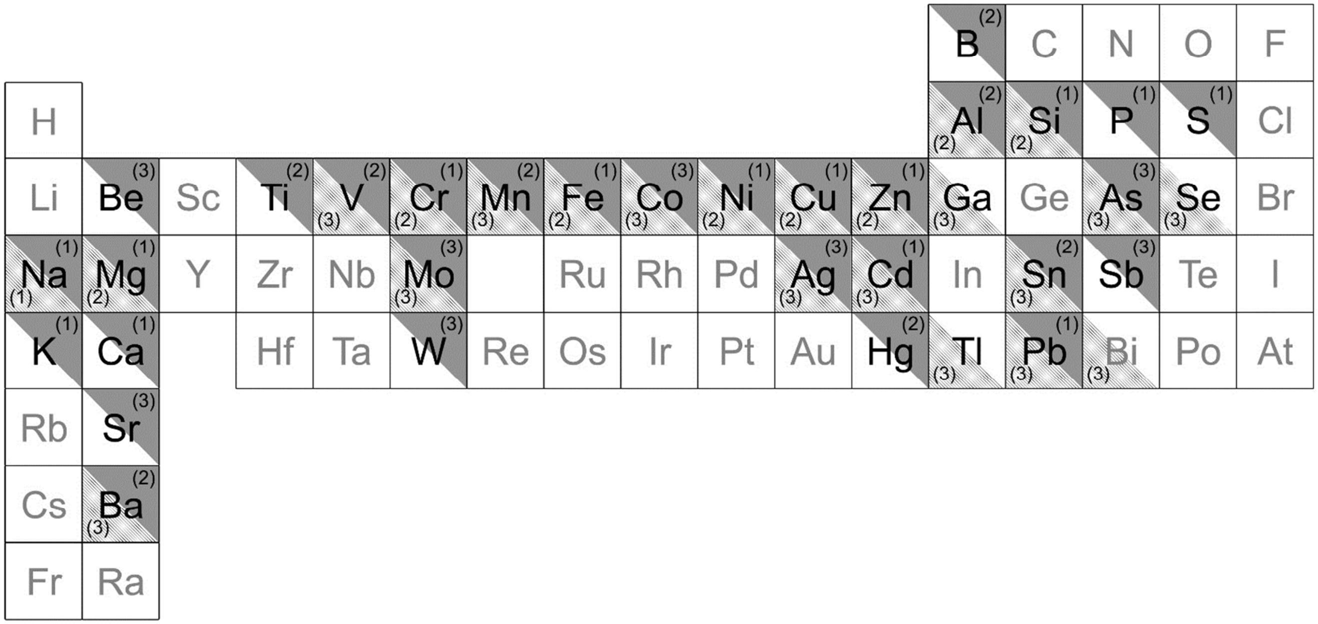

Figure 6~~7~~. Main elements found in real biodiesel and ethanol fuel samples. ■: biodiesel; ░ : bioethanol. (1) Present at concentrations on the order of mg L^{-1}; (2) present at concentrations higher than 10 µg L^{-1} and lower than 1 mg L^{-1}; (3) present at concentrations lower than 10 ng mL^{-1}

Acronym Term	**Term**
AAS	Atomic absorption spectrometry
AFE	Anhydrous fuel ethanol
ANP	National Agency of Petroleum
ASTM	American Society for Testing and Materials
ASV	Anodic stripping voltammetry
BEC	Background equivalent concentration
CA	Continuous aspiration
CDA	Chelidamic acid
CRI	Collision-reaction interface
CV-AFS	Cold vapour atomic fluorescence spectroscopy
ETAAS	Electrothermal atomic absorption spectroscopy
$D_{3,2}$	Sauter mean diameter
D_{50}	Median of the aerosol volume drop size distribution
DCC	dynamic collision cell
DPA	Diphenylamine
DRC	Dynamic reaction cell
ETV	Electrothermal vaporization

FAAS	Flame atomic absorption Spectrometry
FAEE	Fatty acid ethyl esters
FAES	Flame atomic emission spectrometry
FAME	Fatty acid methyl esters
HFE	hydrated fuel ethanol
HR-CS-AAS	High-resolution continuum source graphite furnace atomic absorption spectrometry
IC	Ionic chromatography
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-QQQ	Inductively coupled plasma triple quadrupole
ID	Isotopic dilution
LHR	Solid lignin hydrolysate residue
LOD	Limit of detection
LOQ	Limit of quantitation
MCN	Microconcentric nebulizer
MIP-OES	Microwave-induced plasma optical emission spectrometry

n_e	Electron number density
ORS	Octopole reaction System
PAR	4-(2-pyridylazo)resorcinol
RSD	Relative standard deviation
SF-ICP-MS	Sector field inductively coupled plasma mass spectrometry
SSF	Simultaneous saccharification and fermentation
TEA	Triethylamine
THGA	Transversely heated graphite atomizer
TISIS	Torch Integrated Sample Introduction System
TMAH	Tetramethylammonium hydroxide
USN-MD-ICP-OES	Ultrasonic nebulizer and membrane desolvator inductively coupled plasma optical emission spectrometry
UV	Ultraviolet vacuum
WCAES	Tungsten coil atomic emission spectrometry

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