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**Determination of P, S and Si in biodiesel, diesel and lubricating oil
using ICP-MS/MS**

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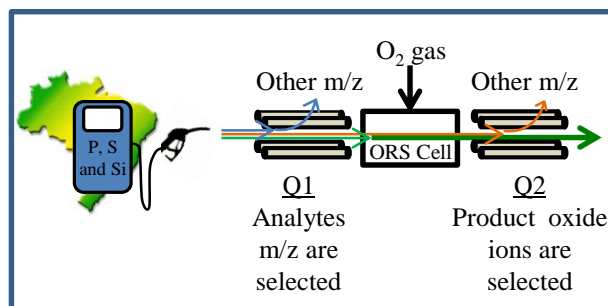
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Graphical Abstract



Abstract

It is demonstrated here the feasibility of the inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) to overcome polyatomic interferences in severely affected isotope determinations. This instrument arrangement presents an octapole reaction/collision system (ORS) in between two quadrupole mass analyzers. The first quadrupole operates as a mass filter which allows just the target mass-to-charge ratio (m/z) to enter the ORS and rejects all other species at m/z different from the target analyte's m/z . Once into the ORS, analyte reacts with reaction gas introduced into the ORS, and the second quadrupole selects the product of reaction m/z (mass shift operation mode). We describe here a procedure for accurate determination of P, S and Si in biodiesel, diesel and lubricating oil by ICP-MS/MS. Fuel standard reference materials (SRMs) were microwave-assisted acid-digested using nitric acid and hydrogen peroxide. The oxygen gas flow rate into the ORS was optimized considering the limit of detection (LOD) values and accuracies reached for P, S and Si determinations in lubricating oil SRM and the best oxygen gas flow rate was 0.75 mL min^{-1} . Adopting optimized conditions, limits of detection were 1.18, 0.49, 0.31, 0.33 and $0.78 \mu\text{g L}^{-1}$ for $^{28}\text{Si}^{16}\text{O}^+$, $^{29}\text{Si}^{16}\text{O}^+$, $^{31}\text{P}^{16}\text{O}^+$, $^{32}\text{S}^{16}\text{O}^+$ and $^{34}\text{S}^{16}\text{O}^+$, respectively. Adequate precision, accuracy and sensitivity were obtained when using the mass shift mode and recoveries for biodiesel, diesel and lubricating oil digests ranged from 89.7 to 102%. No significant differences were observed between the certified values and the ones obtained with the ICP-MS/MS at a 95% confidence level.

Keywords: ICP-MS/MS, spectral interferences, oxide ions, mass shift mode, fuel.

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has been recognized as one of the most powerful and widely applied instrumental technique in analytical chemistry due to the combination of high sensitivity and fast multi-element capabilities.¹ However, since its conception in 1980, there are concerns about spectral overlaps such as from species naturally present in plasma gas and solvents, from isobaric concomitant species and from polyatomic ions formed in the plasma which compromise ICP-MS sensitivity and its accuracy for determination of some elements.^{2,3}

Phosphorus, S and Si are challenging elements to be determined by quadrupole based ICP-MS due to severe polyatomic interferences which affect their main isotopes $^{28}\text{Si}^+$, $^{29}\text{Si}^+$, $^{31}\text{P}^+$, $^{32}\text{S}^+$ and $^{34}\text{S}^+$ caused by $^{14}\text{N}_2^+$, $^{14}\text{N}^{15}\text{N}^+$, $^{14}\text{N}^{16}\text{OH}^+$, $^{16}\text{O}_2^+$, and $^{16}\text{O}^{18}\text{O}^+$, respectively.⁴ These elements are important to be monitored in fuels, since Si based compounds are added in fuel as anti-foaming and P and S are naturally found in fuels and biofuels.^{5,6} The major problems caused by the presence of metals such as Si in fuel are related to the corrosion and damage of the engine parts.⁷ Silicon and P poison the catalysts, even at sub $\mu\text{g mL}^{-1}$ concentrations, decreasing their efficiency to deal with pollutant gases emitted during fuel burn.⁸ Phosphorus and S are both regulated in fuels by governmental agencies around the world due to health and environmental concerns. The emission of S from anthropogenic sources has been related to the depletion of Earth's ozone layer, acid rain incidence and chronic respiratory diseases.^{9,10} European Union and Brazil established the maximum S and P concentrations in diesel and biodiesel in 10 mg kg^{-1} and the ultra low sulfur diesel (ULSD) available in the United States is 15 mg kg^{-1} maximum sulfur concentration.¹¹⁻¹³

The determination of such important and challenging elements requires strategies to overcome polyatomic interferences and to increase the power of detection due to increasingly stricter legislation requirements. Some authors have studied the feasibility of P, S and P oxide ions determinations and, according to them, PO, SO and SiO species are relatively stable.^{14,15}

Under the same conditions, an exothermic reaction will occur faster than an endothermic reaction, the enthalpies of reaction for P^+ and S^+ with O_2 are negative (- 3.17 and - 0.34 eV, respectively), and for Si with O_2 is slightly positive (0.11 eV).¹⁶ Thus, this strategy has been used to determine oxides of these elements in cool plasma conditions,¹⁷⁻¹⁹ and as reaction products using collision and reaction interfaces.²⁰⁻²² Yang and Jiang used a quadrupole-based dynamic and reaction cell (DRC) and O_2 gas flow into the DRC chamber to promote the Si, P and S oxide ions formation to further determinations in steel samples.²⁰ To quantitative analysis of proteins, Wang *et al.* used isotope dilution method by monitoring the $^{32}S^{16}O^+ / ^{34}S^{16}O^+$ ratio by ICP-MS with a hexapole-based collision cell (CC).²¹ The use of octapole reaction system (ORS) also made possible the determination of PO and SO in speciation analysis of barley grain tissues.²² On the other hand, in some cases, the number of interfering ions may increase when compared to the original m/z.^{15,23} For example, shifting the m/z 28 to 44 ($^{28}Si^{16}O^+$), Si determination is still affected by $^{44}Ca^+$, $^{14}N_2^{16}O^+$, $^{12}C^{16}O_2^+$ and $^{88}Sr^{2+}$. The same occurs for sulfur oxides (m/z 48 and 50) affected by $^{48}Ti^+$, $^{36}Ar^{12}C^+$, $^{12}C_4^+$, $^{14}N^{16}O^{18}O^+$, $^{50}Ti^+$, $^{50}Cr^+$, $^{36}Ar^{14}N^+$, $H^{14}N^{35}Cl$ and $^{38}Ar^{12}C^+$, and phosphorus oxide (m/z 47) affected by $^{47}Ti^+$, $^{12}C^{35}Cl^+$, $^{14}N^{16}O_2H^+$ and $^{26}Mg^{18}O^+$.^{4,15} These polyatomic interferences depreciate both accuracy and sensitivity in ICP-MS measurements. Donati *et al.* demonstrated the applicability of the interference standard method (IFS) to determine PO^+ and SO^+ in fuel samples to overcome these interferences in quadrupole based instrument.²⁴

Recently an ICP tandem mass spectrometer (ICP-MS/MS) combining two quadrupole mass filters, Q1 and Q2, and in between them an ORS cell was proposed. This configuration is as an alternative to reduce background signals on analyte oxide m/z and also to improve the accuracy on its determination. Differently from the conventional collision-reaction cell interfaces, in a tandem mass spectrometer configuration there is full control of the ions that enter the cell and consequently the reactions with the gas introduced into the cell are more efficient. The shift mass mode restricts the ions that enter into the ORS cell to a single mass-

to-charge ratio (m/z). Therefore, only selected ions react with the gas inside the cell allowing a better control of the reactions and more efficient collision and reaction interactions inside the ORS. In addition, all ions that present the same m/z as the analyte oxide are rejected at the first quadrupole. The second quadrupole is then set to a specific mass unit. Balcaen *et al.* evaluated this ICP-MS/MS instrument combined to the isotope dilution method to determine low levels of sulfur in ethanol-diluted biodiesel samples.²⁵

In this study, the masses shift of P, S and Si to PO, SO and SiO were evaluated in order to obtain better limits of detection and accuracy. It is demonstrated that the ICP-MS/MS operating in mass shift mode reduced background signals and improved signal-to-background ratios (SBR) even when working with these critical analytes.

Experimental

Instrumentation

An inductively coupled plasma tandem mass spectrometer (ICP-MS/MS, Agilent 8800, Tokyo, Japan) was used to carry out all experiments. The sample introduction system is composed of a Peltier cooled double-pass Scott-type spray chamber, a glass concentric nebulizer, and an one-piece quartz torch with 2.5 mm internal diameter (ID) injector. The ICP-MS/MS operating parameters are shown in Table 1 and both single quadrupole and MS/MS mass shifting mode were used in this study. An Ethos model 1600 microwave oven was used for sample digestion (Milestone, Sorisole, Italy).

Reagents and standard solutions

All solutions were prepared using deionized water (resistivity higher than 18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Nitric acid (Merck, Darmstadt, Germany) previously purified by a sub-boiling distillation system (Milestone) and 30% $m\ m^{-1}$ H₂O₂ (Labsynth, Diadema, SP, Brazil) were used to digest the

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3 samples. Stock monoelement solutions containing 1000 mg L⁻¹ of P, S and Si (Tec-Lab,
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5 Hexis, São Paulo, SP, Brazil) were used to prepare standard reference solutions to build up
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7 the calibration curves by diluting adequate volumes of inorganic standard solutions in 1 % v
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15 **Samples and sample preparation**
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18 Standard reference materials of biodiesel (SRM 2773), diesel (SRM 2723a and SRM
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20 1624d) and lubricating oil (SRM 1848) all from National Institute of Standard and
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22 Technology (NIST, Gaithersburg, MD, USA) and a reference biodiesel sample (B100
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24 Conostan, BaieD’Urfé, Canada) were used to check the accuracy of the method. Sample was
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26 microwave-assisted acid-digested using a cavity oven system. Aliquots of 0.25 g of sample
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28 were accurately weighed directly in Teflon-PFA digestion vessels and 2.5 mL of concentrated
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30 HNO₃ were added to each flask. After a pre-digestion step of 30 min at room temperature, 2.5
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32 mL of distilled-deionized water was added to the mixture. An additional pre-digestion period
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34 of 30 min without any external heating was carried out and 3.0 mL of 30% m m⁻¹ H₂O₂ was
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36 added to each digestion vessel. The microwave-assisted digestion of the samples was then
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38 carried out according to the heating program presented in Table 2. The digestion flasks were
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40 allowed to cool down to room temperature and then, the volume of each solution was made up
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42 to 13.0 mL with distilled-deionized water. The procedure was performed in triplicate for each
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44 sample and further dilution was carried out before analysis to ensure that the concentrations of
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46 the analytes were within the linear dynamic range of the calibration curves and the maximum
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48 concentration of dissolved solids was 0.1% m v⁻¹.
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58 **Results and discussion**
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60 **Detection power and sensitivity**

The analytical performance for each analyte was evaluated in both, single quadrupole ($^{28}\text{Si}^+$, $^{29}\text{Si}^+$, $^{31}\text{P}^+$, $^{32}\text{S}^+$ and $^{34}\text{S}^+$) and MS/MS mode ($^{28}\text{Si}^{16}\text{O}^+$, $^{29}\text{Si}^{16}\text{O}^+$, $^{31}\text{P}^{16}\text{O}^+$, $^{32}\text{S}^{16}\text{O}^+$ and $^{34}\text{S}^{16}\text{O}^+$). Analytical calibration curves ranging from 0.5 to 500 $\mu\text{g L}^{-1}$ were obtained with good linear correlation coefficients (≥ 0.9900) in MS/MS mode. However, it was not possible to obtain linear calibration curves for S and Si isotopes in single quadrupole mode probably due to severe polyatomic interferences on 28, 29, 32 and 34 m/z ratios. When using the MS/MS mode the effect of oxygen gas flow rate into the ORS cell on limits of detection (LOD) and on sensitivity defined as the slope of calibration curves were evaluated. LODs were calculated by using the background equivalent concentrations (BEC), the signal-to-background ratios (SBR) and the relative standard deviations (RSD) for 10 consecutive blank measurements.²⁶ LOD values were calculated as 3 times BEC, multiplied by the RSD, divided by 100. BEC was calculated by dividing the analyte concentration in one of the calibration curve points by its respective signal-to-background ratio (SBR). SBR is the net analytical signal divided by the blank signal.²⁶ Table 3 presents the instrumental LODs and sensitivities obtained in 3 different oxygen gas flow rates. It is important to note that the instrumental LODs for S determination observed here were even lower than 3.5 $\mu\text{g L}^{-1}$ S obtained using isotope dilution method and sector field-ICP-MS (SF-ICP-MS) described by Amais *et al.*²⁷ Better LOD was also observed for Si compared to that established by Neves *et al.* in direct analysis of ethanol fuel (14 $\mu\text{g L}^{-1}$) by ICP-MS equipped with collision and reaction interface (CRI) and also for P determination compared to oxide ion detection in cool plasma ICP-MS (0.4 $\mu\text{g L}^{-1}$).^{28,15} In addition, considering the sample dilution factor due to sample preparation step, limits of detection at 0.75 mL min⁻¹ O₂ gas flow rate into the ORS were 1.23, 0.51, 0.32, 0.34 and 0.81 $\mu\text{g g}^{-1}$ for $^{28}\text{Si}^{16}\text{O}^+$, $^{29}\text{Si}^{16}\text{O}^+$, $^{31}\text{P}^{16}\text{O}^+$, $^{32}\text{S}^{16}\text{O}^+$ and $^{34}\text{S}^{16}\text{O}^+$, respectively.

One advantage of the strategy is that, although the slope of calibration curves decreased when higher oxygen gas flow rate was introduced into the ORS³ cell, the LODs were not depreciated. In addition, considering Si natural isotope abundance, ^{28}Si 92.23 % and

^{29}Si 4.67%, the high sensitivity on $^{29}\text{Si}^{16}\text{O}^+$ was not previously expected at 0.75 mL L⁻¹ O₂ gas flow rate. However, since the Q1 selects m/z 29 which means $^{29}\text{Si}^+$ and also $^{28}\text{SiH}^+$, it is possible that the high oxygen gas flow rate increases the $^{28}\text{Si}^{16}\text{OH}^+$ formation and this specie is selected by Q2 mass analyzer.

Considering the maximum S and P concentrations in diesel and biodiesel established by Brazilian and European Union (10 mg kg⁻¹) and the dilution factor of digestates due to low residual acidity and dissolved carbon content, the limits of detection reached using the developed procedure attend the legislative requirements. The official recommended methods by National Agency of Petroleum, Natural Gas and Biofuels (ANP) in Brazil and European Union for sulfur determination in diesel to attend the requirements of S legislations are ultraviolet fluorescence spectrometry (UV fluorescence) and wavelength dispersive X-ray fluorescence (WDXRF) spectrometry, but it is here demonstrated that simultaneous P, S and Si determinations can be performed by ICP-MS/MS and sensitivities reached may support the gradual decrease of P, S and Si concentrations allowed in diesel and biodiesel by governmental requirements based on environmental aspects.²⁹

Accuracy of the procedure

The accuracy of the procedure for P, S, and Si determinations in lubricant oil samples using MS/MS mode was evaluated comparing certified values of lubricating oil SRM 1848 and determined concentrations (Table 4) in different O₂ gas flow rates. Considering all studied oxide ions formed from the P, S and Si isotopes, best recoveries were obtained when introducing 0.75 mL min⁻¹ O₂ into the ORS cell. Adopting this condition, all analytes evaluated presented recoveries ranging from 89.7 to 102% indicating the efficiency of MS/MS mode to overcome polyatomic interferences that damage P, S and Si determinations. Except for $^{29}\text{Si}^{16}\text{O}^+$, 0.50 mL min⁻¹ oxygen gas flow rate is also an effective condition for accurate P, S and Si determinations in digested fuel samples. For both O₂ gas flow rates, 0.50

and 0.75 mL min^{-1} , no statistically significant difference was observed between certified and determined values by applying a t-test at a 95% confidence level.

The accuracy of the procedure was also demonstrated for P, S and Si determinations in biodiesel and diesel samples. Table 5 shows the S determination in biodiesel and diesel SRMs and also in a reference biodiesel sample. Recoveries ranging from 100 to 111% were observed and sulfur determined concentrations are adequate since no significant differences at a 95% confidence level were observed among the certified values and the ones obtained using the ICP-MS/MS, except for $^{32}\text{S}^{16}\text{O}^+$ in Conostan reference biodiesel sample. Because P and Si in biodiesel and diesel are not certified in the SRMs analyzed, a spike experiment was carried out for these analytes. In this case, $10 \mu\text{g L}^{-1}$ of P and Si in biodiesel and diesel were added to digested samples (Table 6). Determined values are in agreement with added concentrations and recoveries ranging from 90.8 to 117% were observed, except for $^{28}\text{Si}^{16}\text{O}^+$ in SRM 1624d and SRM 2773. Better recoveries in addition and recovery experiments for Si determination in diesel and biodiesel were observed by monitoring m/z 45 ($^{29}\text{Si}^{16}\text{O}^+$) probably because the sensitivity at $^{29}\text{Si}^{16}\text{O}^+$ is 29-fold higher than by monitoring m/z 44 ($^{28}\text{Si}^{16}\text{O}^+$).

One great advantage of this instrument configuration is that in a conventional quadrupole-based ICP-MS equipped with a reaction cell, the $^{32}\text{S}^{16}\text{O}^+$ product ion at m/z 48 would be overlapped by isobaric interferences, such as $^{48}\text{Ca}^+$, $^{48}\text{Ti}^+$ or $^{40}\text{Ar}^{12}\text{C}^+$, however these species were rejected by the first quadrupole in ICP-MS/MS, which allows accurate and sensitive determination of ^{32}S in complex matrices. Another advantage of the ICP-MS/MS is the use of oxygen as a reaction gas to remove interferences. Before this instrumental arrangement, the use of oxygen had been limited to determination of a small number of analytes in simple matrices in ICP-QMS because oxygen can react with matrix components, analytes and polyatomic species in the cell producing new and undesirable interferences and/or losses of analyte.

Conclusions

The determination of the oxide ions of P, S and Si using Agilent 8800 ICP-MS/MS by adding oxygen gas into the ORS cell (MS/MS mode) was demonstrated as an effective alternative to overcome spectral interferences on their m/z ratios without compromising limits of detection or precision of the method, even in complex matrices. Results obtained were in excellent agreement with certified values, proving the accuracy of the developed procedure.

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Tables

Table 1. Agilent 8800 ICP-MS/MS operating conditions.

Instrument parameter	Operating condition
RF applied power (W)	1550
Plasma gas flow rate (L min ⁻¹)	18
Auxiliary gas flow rate (L min ⁻¹)	1.8
Carrier gas flow rate (L min ⁻¹)	1.08
Signal acquisition time (s)	3
Sampling depth (mm)	8
Number of replicates	3
Stabilization time (s)	10
Cell gas	O ₂
Nebulizer	Concentric nebulizer - glass
Spray chamber	Scott type - double pass
Spray chamber temperature (°C)	2
Selected mass at Q1	28, 29, 31, 32 and 34
Selected mass at Q2	44, 45, 47, 48 and 50

Table 2. Heating program used in the microwave-assisted acid-digestion of lubricating oil samples.

Step	Applied power (W)	Time (min)	Temperature (°C)
1	250	2	80
2	0	3	80
3	550	4	120
4	650	5	180
5	750	5	200

Table 3. Limits of detection and sensitivities for P, S and Si in different oxygen gas conditions by MS/MS mode.

Product of reaction	0.30 mL min ⁻¹ O ₂		0.50 mL min ⁻¹ O ₂		0.75 mL min ⁻¹ O ₂	
	LOD (µg L ⁻¹)	Sensitivity ^a	LOD (µg L ⁻¹)	Sensitivity ^a	LOD (µg L ⁻¹)	Sensitivity ^a
²⁸ Si ¹⁶ O ⁺	1.0	1832	0.72	354	1.2	42.9
²⁹ Si ¹⁶ O ⁺	0.79	1262	0.75	384	0.49	1265
³¹ P ¹⁶ O ⁺	0.05	1366	0.02	943	0.31	235
³² S ¹⁶ O ⁺	0.46	1771	0.52	1496	0.33	346
³⁴ S ¹⁶ O ⁺	0.94	86.4	1.2	73.1	0.78	21.6

^a Sensitivity defined as the slope of analytical calibration curves (counts.L.s⁻¹.µg⁻¹)

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Table 4. Phosphorus, S and Si determinations in lubricant oil (SRM 1848) by ICP-MS/MS in mass shift mode (n = 3).

	Reference	Isotope	Single quad mode	Product of	0.30 mL min ⁻¹	Rec.	0.50 mL min ⁻¹	Rec.	0.75 mL min ⁻¹	Rec.
	(mg kg ⁻¹)			reaction	O ₂	(%)	O ₂	(%)	O ₂	(%)
Si	50 ± 2 ^a	²⁸ Si	c	²⁸ Si ¹⁶ O ⁺	44 ± 2	87.2	48 ± 2	96.4	54 ± 3	107.1
		²⁹ Si	c	²⁹ Si ¹⁶ O ⁺	-	-	41 ± 4	82.6	47 ± 4	95.0
P	7880 ± 280 ^b	³¹ P	397 ± 33 / 5.45% rec.	³¹ P ¹⁶ O ⁺	8370 ± 510	106	7650 ± 120	97.1	7570 ± 310	96.1
S	23270 ± 43 ^b	³² S	c	³² S ¹⁶ O ⁺	26450 ± 730	114	24010 ± 820	103	23850 ± 910	102.2
		³⁴ S	c	³⁴ S ¹⁶ O ⁺	25900 ± 1570	111	23985 ± 830	103	23800 ± 840	102.2

^aReference value. ^bCertified value. ^c No calibration curve was obtained.

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Table 5. Sulfur determination in diesel and biodiesel SRM by ICP-MS/MS using $0.75 \text{ mL min}^{-1} \text{ O}_2$ into the ORS cell ($n = 3$).

Samples	Certified value (mg kg^{-1})	$^{32}\text{S}^{16}\text{O}^+$		$^{34}\text{S}^{16}\text{O}^+$	
		Determined	Recovered (%)	Determined	Recovered (%)
Diesel - SRM 2723a	10.96 ± 0.31	11.2 ± 0.7	102	11.7 ± 0.7	106
Diesel - SRM 1624d	3882 ± 20	4000 ± 230	103	4020 ± 240	103
Biodiesel - SRM 2773	7.39 ± 0.39	8.3 ± 0.5	113	8.2 ± 0.6	111
Biodiesel B100 Conostan	100^a	108 ± 2	108	100 ± 3	100

^aReference value

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Table 6. Addition and recovery experiments for P and Si in diesel and biodiesel SRM by ICP-MS/MS using 0.75 mL min⁻¹ O₂ into the ORS cell (n = 3).

Sample	Added (µg L ⁻¹)	²⁸ Si ¹⁶ O ⁺		²⁹ Si ¹⁶ O ⁺		³¹ P ¹⁶ O ⁺	
		Determined	Recovered	Determined	Recovered	Determined	Recovered
			(%)		(%)		(%)
Diesel - SRM 2723a	10	10.7 ± 0.2	107	9.3 ± 0.2	93	10.4 ± 0.3	104
Diesel - SRM 1624d	10	13.5 ± 1	135	9.6 ± 1	96	9.1 ± 2	91
Biodiesel - SRM 2773	10	12.1 ± 0.5	121	10.9 ± 0.4	109	11.6 ± 0.4	116
Biodiesel B100 Conostan	10	11.0 ± 1	110	9.2 ± 0.8	92	11.7 ± 0.8	117

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