Direct Elemental Analysis of Biodiesel by 7500ce ICP-MS with ORS

Application Note

Petrochemical

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Abstract

A simple and sensitive method is described for the measurement of multiple trace elements in a range of biofuels using an Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS) featuring the Octopole Reaction System (ORS). Each sample was analyzed directly following a simple dilution in kerosene. The ORS effectively removes matrix and plasma-based spectral interferences to allow measurement of all important analytes, including sodium, potassium, lead, vanadium, and sulfur, at levels lower than those possible by ICP-optical emission spectroscopy (OES). The detection limits (DLs) and background equivalent concentrations (BECs) were in the µg/kg (ppb) range for all elements except sulfur (mg/kg). Good spike recovery is presented for a rapeseed biodiesel sample and petrochemical diesel (between 90 and 120%, with the majority of elements within 5% of the target value). A 10-hour stability test using a spiked (approx 10 µg/kg) rapeseed material yielded excellent precision for almost all elements (between 6.4% for boron and 1.3% for arsenic). The results show that the 7500ce methodology can be used for the routine measurement of trace metals in biofuels.

Introduction

Biodiesel is a renewable fuel derived from natural oils that can be used in diesel-engine vehicles with little or no modification. Biodiesel refers to a collection of alkyl esters derived from renewable or “bio” sources such as cooking oils, animal fats, or plant oils. In its pure form it is termed fatty acid methyl ester (FAME). Commercial biodiesel is usually a blend of the pure FAME and fossil-fuel petrochemical diesel. The blend ratio is given as its B number, for example, B5 (5% FAME 95% petro); B100 (100% FAME).

Elements of interest are catalyst residues (usually Na and K), sulfur due to emission legislation and the low sulfur requirements of modern diesel engines, and catalyst poison elements such as lead, vanadium, and mercury. Although lead, vanadium, and mercury tend to be naturally low in the raw oil stock, they can still be found in the final product from contamination during oil processing or final FAME production. Common fuel additives include silicon (anti-foaming agent), manganese (burn improver), and other specialist materials such as additives for marine applications (chromium, iron, and nickel products). These elements need to be monitored to ensure correct dosage. Traditional analytical techniques for analysis of biofuels are ICP-optical emission spectroscopy (OES) and atomic absorption spectroscopy (AAS/FAAS). However, these techniques suffer from intense interferences due to an increased background continuum from the carbon matrix, so they are limited to a few elements or have limited detection limits.

Experimental

Standards and internal standards were prepared from ~1,000 mg/kg metallo-organic oils (Spex Certiprep, Metuchen, New Jersey, USA, and Conostan, Conoco-Phillips, Bartlesville, OK, USA). Internal standards were added to all samples and standards prior to analysis to compensate for viscosity differences. Samples and standards were prepared by simple 3x dilution in kerosene (Purum, Fluka Sigma-Aldrich, St. Louis, USA) using weight/weight preparation. Five samples were analyzed: processed soybean and rapeseed oils, pork and poultry tallow (both B100), and petrochemical diesel taken from a local gasoline station.

An Agilent 7500ce ICP-MS fitted with an Octopole Reaction System (ORS) for removal of polyatomic interferences was used for this study. The instrument was operated using hydrogen, helium, xenon, and no-gas cell modes. All modes were acquired sequentially during a single visit to the sample vial. Instrumental conditions are given in Table 1.

Table 1. 7500ce ICP-MS Operating Conditions

Forward power	1550W
Plasma gas	15 L/min
Auxillary gas	1 L/min
Sampling depth	8 mm
Carrier gas	0.9 L/min
Oxygen (50% O_2 in Ar)	0.12 L/min
ORS Cell Gas Flow Rates	
Helium (He)	5.7 mL/min
Hydrogen (H_2)	6.5 mL/min
Xenon (Xe)	0.54 mL/min

The ORS operating in helium collision mode removes polyatomic interferences using a process known as kinetic energy discrimination (KED). The larger interfering species experience more collisions with He atoms and lose energy as they pass through the cell. An energy differential is applied to prevent the lower energy polyatomic ions from entering the mass filter. Reaction mode using hydrogen gas was used to remove the intense plasma-based species such as $^{14}N_2$ on ^{28}Si, $^{38}Ar^1H$ on ^{39}K, and ^{40}Ar on ^{40}Ca. The interference is neutralized or converted to another species by reaction. Finally, sulfur can be measured most effectively by removing the O_2 interference by reaction with Xe cell gas using a third cell gas controller (Agilent product number G3264A). For interference-free analytes, the cell can be operated in no-gas mode, that is, with no cell gas added to the ORS cell. Oxygen was added to the plasma by an additional mass flow controller (Agilent product number G3145B) to remove excess carbon from the plasma and to prevent it from condensing on the interface and ion lenses; this was used in conjunction with the organic solvent introduction kit (Agilent product number G1833-65038). Note that, while a 50% O_2 in argon mix was used for this application, a 20% O_2 in argon mix is the preferred option, as this provides more precise control of the O_2 flow rate, which may be critical in certain applications, such as low-level S and P analysis.

Results and Discussion

Detection limit (DL) and background equivalent concentration (BEC) for the kerosene diluent and a diluted soy B100 sample are given in Table 2. The DLs and BECs were in the µg/g (ppb) range for all elements except sulfur (mg/kg). The calibration profiles for vanadium (Figure 1) were obtained with and without cell gas. The large offset for the calibration graph in no-gas mode (due to matrix interference) is removed by the ORS in helium mode. Figure 2 shows a calibration plot for ^{32}S in Xe gas mode, demonstrating the effective removal of the O_2 interference by the ORS.

Tables 3 and 4 show the analytical results, including spike recoveries for rapeseed FAME and petrochemical diesel. Recoveries for all elements were between 90 and 120%, but the majority fell within 5% of the target value. This indicates reliable interference removal for the spiked matrices and the applicability of the technique for trace and ultratrace determination of metallic impurities. The data for sodium is particularly high for the B100 rape oil and pork tallow samples; this is an indication of inadequate cleanup procedures of the final FAME product.

Table 2. Detection Limits (3s) and Background Equivalent Concentrations (BEC) for Kerosene Solvent and 3x Diluted B100 Soy FAME Data Reported as µg/kg (S as mg/kg)

			Kerosene		**B100 Soy**					**Kerosene**		**B100 Soy**	
Element	**Mass**	**Mode**	**DL**	**BEC**	**DL**	**BEC**	**Element**	**Mass**	**Mode**	**DL**	**BEC**	**DL**	**BEC**
Be	9	NoGas	0.0153	0.0234	0.0109	0.0423	Ni	60	He	0.0250	0.0367	0.126	0.165
B	10	NoGas	0.344	4.63	6.57	30.1	Cu	63	He	0.0525	0.681	0.0264	0.832
Na	23	NoGas	2.99	18.8	1.19	62.5	Cu	65	He	0.0723	0.675	0.101	0.834
Mg	24	H_2	1.37	8.90	8.65	9.77	Zn	66	He	0.0393	0.0685	0.211	0.963
Si	28	H_2	5.17	53.3	7.44	48.7	As	75	He	0.0896	0.192	0.0660	0.547
P	31	He	10.0	52.0	22.7	811	Sr	88	NoGas	0.0335	0.121	0.0631	0.215
S	32	Xe	0.124	0.569	0.0293	0.980	Mo	95	NoGas	0.500	0.411	0.371	0.332
K	39	H_2	0.649	1.34	2.10	7.25	Ag	107	NoGas	0.0374	0.0832	0.149	0.155
Ca	40	H_2	0.568	2.95	6.40	9.21	Cd	111	NoGas	0.121	0.138	0.108	0.0913
Ti	47	He	0.125	0.0396	0.706	0.680	Sn	118	NoGas	0.0173	0.0901	0.411	84.8
V	51	He	0.0198	0.0435	0.0409	0.134	Sb	121	NoGas	0.0261	0.0827	0.0395	0.0895
Cr	52	H_2	0.0935	0.0772	0.0224	0.402	Ba	137	NoGas	0.0472	0.145	0.0990	1.87
Mn	55	He	0.0249	0.0527	0.0563	0.101	W	182	NoGas	0.0111	0.0231	0.0177	0.0261
Fe	56	He	0.0447	0.129	0.0869	4.21	Hg	201	NoGas	0.0147	0.107	0.123	0.403
Co	59	He	0.0113	0.0245	0.0337	0.0400	Pb	208	NoGas	0.00724	0.0595	0.0226	0.0666

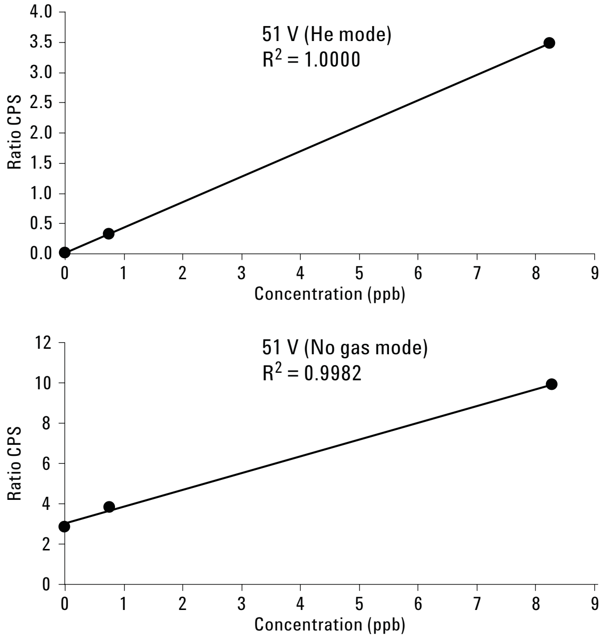

Figure 1. Calibration plots for ^{51}V in helium gas mode (top) and no-gas mode (bottom) demonstrating effective interference removal by the ORS.

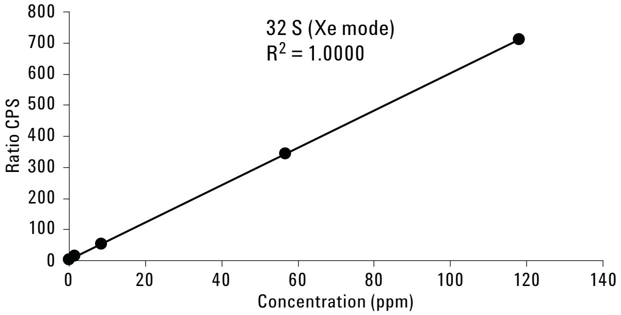

Figure 2. Calibration plot for ^{32}S in Xe gas mode.

Table 3. Analytical Data B100 FAME and a Petrochemical Diesel Sample (Corrected for Dilution Factor)

Element	Mass	Mode	Units	B100 rape	B100 soy	B100 poultry	B100 pork	Petrodiesel
Na	23	He	µg/kg	1,040	127	1,430	614	20.0
K	39	H_2	µg/kg	15.4	19.1	50.6	22.4	6.28
S	32	Xe	mg/kg	3.20	1.29	15.9	18.9	9.85
Be	9	NoGas	µg/kg	0.0609	0.0681	0.0241	0.0202	N/D
B	10	H_2	µg/kg	40.3	81.2	334	54.6	5.08
Mg	24	H_2	µg/kg	8.57	6.16	12.1	7.69	6.80
Si	28	H_2	µg/kg	39.8	6.02	8,220	159	372
P	31	He	µg/kg	21.4	2,120	171	85.5	28.5
Ca	40	H_2	µg/kg	131	20.8	135	26.8	2.57
Ti	47	He	µg/kg	0.342	2.01	8.08	2.45	0.0798
V	51	He	µg/kg	0.186	0.302	1.36	0.310	N/D
Cr	52	H_2	µg/kg	1.36	1.04	0.718	0.394	0.446
Cr	53	H_2	µg/kg	1.09	0.939	0.765	0.376	0.390
Mn	55	He	µg/kg	0.450	0.170	0.364	0.114	0.190
Fe	56	He	µg/kg	4.61	12.3	50.8	5.21	30.5
Co	59	He	µg/kg	0.0449	0.0578	0.124	0.0856	N/D
Ni	60	He	µg/kg	3.64	0.416	0.816	0.397	0.239
Cu	63	He	µg/kg	3.28	0.730	11.5	5.49	2.09
Cu	65	He	µg/kg	3.23	0.752	11.5	5.64	2.12
Zn	66	He	µg/kg	17.9	2.80	27.4	7.74	47.0
As	75	He	µg/kg	1.29	1.18	1.08	1.02	0.145
Sr	88	NoGas	µg/kg	4.59	0.339	3.47	0.583	N/D
Mo	95	NoGas	µg/kg	0.263	N/D	N/D	N/D	N/D
Ag	107	NoGas	µg/kg	0.563	0.257	3.15	0.617	0.0527
Cd	111	NoGas	µg/kg	0.304	N/D	0.589	N/D	N/D
Sn	118	NoGas	µg/kg	N/D	131	1.71	0.138	N/D
Sb	121	NoGas	µg/kg	0.0920	0.0528	0.399	0.109	N/D
Ba	137	NoGas	µg/kg	14.6	5.35	55.8	4.64	N/D
W	182	NoGas	µg/kg	0.121	0.0181	0.112	0.0252	N/D
Hg	201	NoGas	µg/kg	0.582	0.404	0.396	0.791	N/D
Pb	208	NoGas	µg/kg	0.372	0.0450	0.385	0.0693	0.191

Table 4. Spike Recovery Data for a Rape FAME and Petrochemical Sample – Spiked with a Multielement Mixed Concentration Solution – Recoveries Are Presented as %

Sample	Mass	Mode	Units	B100 rape	Rape spike	% recovery	Diesel spike	% recovery
Na	23	He	µg/kg	1,040	Spike too low	197	105	
K	39	H_2	µg/kg	15.4	185	98.2	172	98.5
S	32	Xe	mg/kg	3.20	13.1	101	18.3	108
Be	9	NoGas	µg/kg	0.0609	164	94.9	164	97.3
B	10	H_2	µg/kg	40.3	207	96.8	170	103
Mg	24	H_2	µg/kg	8.57	170	93.6	154	87.1
Si	28	H_2	µg/kg	39.8	202	94.0	Spike too low	–
P	31	He	µg/kg	21.4	211	110	234	122
Ca	40	H_2	µg/kg	131	285	89.2	169	98.7
Ti	47	He	µg/kg	0.342	165	95.5	164	97.1
V	51	He	µg/kg	0.186	170	98.4	172	102
Cr	52	H_2	µg/kg	1.36	171	98.2	169	100
Cr	53	H_2	µg/kg	1.09	167	96.0	163	96.4
Mn	55	He	µg/kg	0.450	167	96.7	168	99.7
Fe	56	He	µg/kg	4.61	182	103	184	90.9
Co	59	He	µg/kg	0.0449	184	101	185	110
Ni	60	He	µg/kg	3.64	193	110	191	113
Cu	63	He	µg/kg	3.28	198	113	200	117
Cu	65	He	µg/kg	3.23	198	113	201	118
Zn	66	He	µg/kg	17.9	225	120	250	121
As	75	He	µg/kg	1.29	230	133	227	108
Sr	88	NoGas	µg/kg	4.59	175	98.9	172	102
Mo	95	NoGas	µg/kg	0.263	161	99.9	164	97.1
Ag	107	NoGas	µg/kg	0.563	183	106	197	117
Cd	111	NoGas	µg/kg	0.304	198	115	200	118
Sn	118	NoGas	µg/kg	N/D	165	95.8	168	99.6
Sb	121	NoGas	µg/kg	0.0920	169	97.9	173	102
Ba	137	NoGas	µg/kg	14.6	172	91.2	156	92.7
W	182	NoGas	µg/kg	0.121	159	97.5	173	102
Hg	201	NoGas	µg/kg	0.582	Not in spike mix	–	–	–
Pb	208	NoGas	µg/kg	0.372	157	90.5	170	100

Instrumental stability was tested for 10 hours using a spiked (approximately 10 µg/kg) rapeseed material. Repeatability over the 10-hour run varied between 6.4% for boron to 1.3% for arsenic, indicating good reproducibility for an extended sample set; the normalized stability plot is displayed in Figure 3.

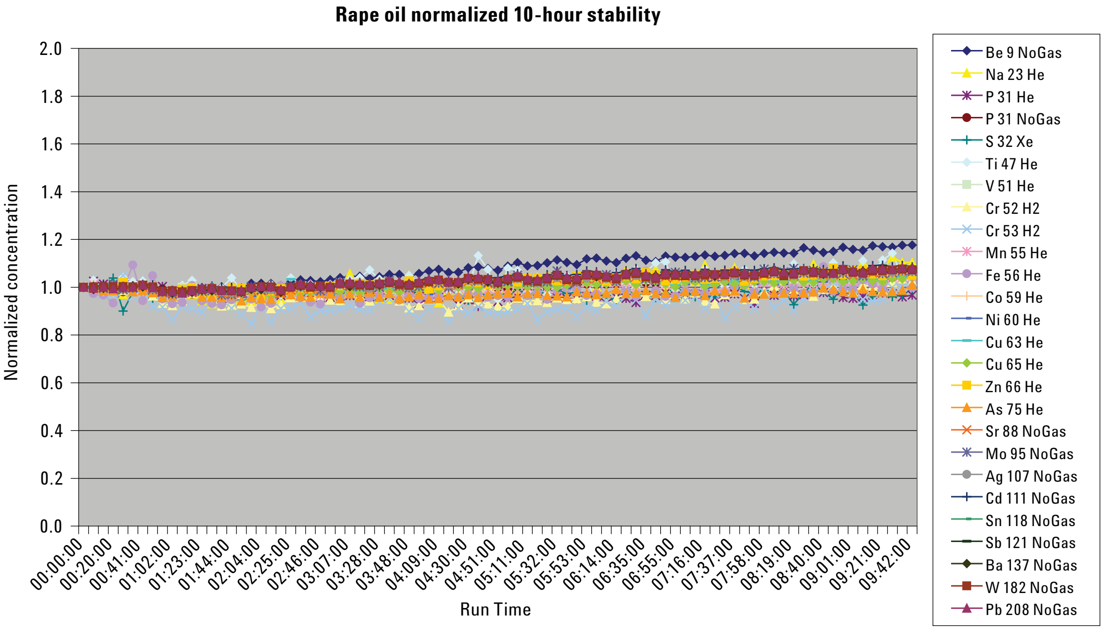

Figure 3. **Normalized stability plot for 3x diluted rapeseed B100 biodiesel. Sample diluted in kerosene and run repeatedly over a 10-hour period.**

Conclusions

The methodology outlined shows that the 7500ce ICP-MS is suitable for the routine analysis of biofuels following a simple dilution step in kerosene. The use of the ORS in the appropriate gas mode efficiently removes plasma-based and matrix-based interferences, improving detection limits for all key elements compared to ICP-OES. (BECs were generally limited by background contaminant levels). The 7500ce also offers a wider elemental coverage compared to ICP-OES and AAS, which are typically used for determining a limited elemental suite in FAME. The lower backgrounds and greater dynamic range and predictability of interferences simplify the analysis significantly.

NOTE: The 7500ce has now been superseded by the 7500cx. For this application, the 7500cx should be fitted with the optional H_2 cell gas line (and low flow third cell gas line if sulfur is to be measured).

References

The full paper of this work was originally published in *Analytical and Bioanalytical Chemistry* (2007) 389:753-761. The publication is also available online at www.springerlink.com: "Direct elemental analysis of biodiesel by inductively coupled plasma-mass spectrometry," (DOI 10.1007/s00216-007-1439-0).

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