

Metals Determination in Biodiesel (B100) by ICP-OES with Microwave Assisted Acid Digestion

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Abstract: Elemental composition of biodiesel is required for product quality-control, auto-engine life, emissions control, and researching appropriate additives. The use of microwave assisted acid digestion reaction system to prepare neat biodiesel (B100) samples in an aqueous medium for simultaneous inductively coupled plasma optical emission spectrometer (ICP-OES) analyses is reported. Biodiesel produced by transesterification reaction was subjected to the test method using calibration standards prepared in an aqueous medium. Significant correlation for the spiked B100 samples, instrument detection limits, accuracy, and precision data showed that elemental concentrations can easily be determined within the specified limits. The method avoids switching any of the ICP-OES accessories required for high organic loads. This method is most appropriately devised for biodiesel analysis than petrochemicals analysis.

Keywords: Biodiesel, transesterification, metals analysis, B100, microwave digestion, ICP-OES, fatty acid methyl esters, ASTM, auto-emissions.

1. INTRODUCTION

The rising cost and environmental impacts associated with petroleum-based fuels has led to the exploration of a renewable alternative fuel – Biodiesel. Biodiesel, defined as a mixture of mono-alkyl esters, is produced from a wide range of vegetable oils and animal fats more commonly by a lipid transesterification process [1-3]. Biodiesel can be substituted for petroleum-based diesel fuel (petrodiesel) in virtually any standard unmodified diesel engine [4, 5]. Pure biodiesel or biodiesel blended with petroleum diesel can be used to fuel diesel vehicles, providing energy security and emissions and safety benefits.

A consistent quality assurance program is necessary to avoid performance issues in vehicle engines and to ensure sustainable growth of biodiesel production. Inorganic constituents in the final product can promote residue build up in the engine, cause corrosion and ultimately affect engine life. Elements introduced during production process (Na, K, Ca, and Mg) are of particular concern, while other elements present in the feedstock (P, S, and Zn), or used as additives (Si, Mn, Cr, Fe, and Ni) require monitoring in order to avoid undesirable combustion products in the engines [6]. Since metallic elements in fuel are undesirable even at lower concentrations, their determination in fuel is necessary to evaluate fuel quality, to see their effect on auto engines, and to control environmental pollution.

1.1. Significance of Metals Analyses

Since the concentration of metals in biodiesel is generally low, the use of highly sensitive analytical techniques is

required. The American Society for Testing and Material (ASTM) and European Standards Organization (EN) have developed specifications, ASTM D6751 and EN 14214 respectively [7, 8] to test pure biodiesel (B100) by physical, chromatographic, and spectroscopic methods to apply the standards. ASTM D4951 and EN 14538 methods are used to analyze biodiesel samples for trace metals [9, 10]. The method only requires sodium, potassium, calcium, magnesium, phosphorus, and sulfur since the presence of these metals contaminants can lead to operational problems in vehicle engines. Sodium and potassium hydroxides are important as they are utilized as catalysts in the production process of biodiesel and are removed during the wash process. Presence of these metals in the final product can result in the formation of deposits in the fuel injection system as well as poisoning of emission control after-treatment systems. Magnesium and calcium, though rarely used as absorbents in the production process, can cause similar problems in vehicle engines as sodium and potassium. Phosphorus can also form deposits and damage the ability of after-treatment systems to reduce exhaust emissions. Sulfur levels in fuel are reduced to 0.0015% (or 15 mg/L). Biodiesel or their blends are not supposed to exceed this limit. Metals other than those discussed above, are important as further research is conducted to see the effects of additives and chemicals on the physical and chemical characteristics of biodiesel. This method allows for convenient determination of the concentrations of metals in biodiesel samples. This method might be of special interest to environmental laboratories who analyze samples of varying matrices on the same instrument using the same accessories and similar instrument conditions; hence avoiding the use of additional gases to oxidize organic contents in the samples or changing accessories.

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1.2. Current Practices of Metals Analyses in Biodiesel

The ASTM 4951 method calls for weighing a portion of sample diluted by mass with mixed xylenes or other solvent. The solutions are introduced to the inductively coupled plasma (ICP) instrument by free aspiration. Increased organic content in the sample can increase carbon build-up on the quartz torch and may affect the performance of the instrument in subsequent samples. Carbon accumulation on the tip of the torch injector tube is a general problem associated with samples containing high levels of organics or organic solvents. Therefore, a nebulizer gas consisting of oxygen, usually 1% in argon, is used to remove the carbon deposits (method ASTM 4951). A separate sample introduction system, including torch, gas, chamber, nebulizer, and lines, is maintained for such samples. The sample introduction system is generally switched whenever samples other than biodiesel are required to run. This paper is an attempt to reveal that the same instrument conditions and accessories could be used for most samples in aqueous medium where the ICP-optical emission spectroscopy (ICP-OES) is the first choice of instrumentation. These findings could hence save time and cost associated with switching the accessories without compromising the response and sensitivity of the instrument. This method is more appropriately devised for biodiesel analysis than petrochemicals analysis.

Edlund *et al.* 2002 [11] investigated the addition of oxygen to the gases of the ICP to avoid carbon deposits on the torch or to reduce the background emission for the analysis of biodiesel samples. The oxygen addition was found to be useful for the determination of sodium (Na), because of the suppression of the strong molecular bands of carbon compounds close to the intense Na lines at 588 and 589 nm.

1.3. Problems in Current Practices

Due to the immiscible nature of biodiesel in water, a dedicated sample introduction system (torch, spray chamber, sampling probe, and tubing) has to be used for biodiesel samples. The instrument has to be calibrated separately for water and biodiesel samples. This act becomes extremely cumbersome for labs with a large number of samples and a limited number of instruments. In this situation it will be helpful to use a uniform water-based procedure which, regardless of the sample matrix, can be used simultaneously. The high pressure associated with the use of solvents in conventional methods results in gradual accumulation inside the spray-chamber with time, which can cause the plasma to flicker and affect signal stability. Problems associated with the direct introduction of biodiesel or its blends in the ICP plasma include the production of flames leading to destabilization or extinction of the plasma and the deposition of carbon residues on the torch and cone. Regardless of the instrument used, appropriate sample pretreatment is most critical for determining the accuracy of the analysis. Errors associated with this stage will significantly affect the final results. Onyeso 2005a, 2005b [12, 13] developed a method for the determination of Manganese (Mn) in gasoline and diesel fuel by ICP-OES after digestion of the samples in a microwave oven and dilution with water before direct aspiration into the plasma.

2. MATERIAL AND METHODS

2.1. Biodiesel Production

Biodiesel was produced in an automatic biodiesel processor, BioPro 190 (AGR Energy, Chico, CA, USA)). The process involved esterification and transesterification of used canola oil with methanol using H_2SO_4 and KOH as acid and base catalysts, respectively. The oil was filtered through a 400 micron filter before processing. The oils with the free fatty acid content of approximately 2.98% (determined by acid-base titration) were converted into esters (biodiesel) by a reaction with methanol using acid catalyzed esterification (H_2SO_4). This reaction was followed by a base-catalyzed transesterification reaction using methanol and KOH to convert triglycerides (vegetable oil) into fatty acid methyl esters, FAMES (biodiesel). Methanol and KOH were mixed to form methoxide which was then introduced to the triglycerides along with vigorous agitation at approximately 60 °C. The reaction mixture was allowed to settle for 20 h. Glycerol was formed as a by-product and was separated from biodiesel, settling at the bottom. The biodiesel product was washed with tap water and filtered sequentially through 10 and 2 micron filters. The final product was tested according to ASTM procedures for total and free glycerin (ASTM D6751).

2.2. Samples Preparation

Six sets of B100 samples in triplicate were prepared by weighing 0.25–0.5 g of biodiesel up to four decimal places into acid-rinsed fluorocarbon digestion vessels. The vessels were supplied with single ported Teflon caps equipped with pressure relief valves to regulate excessive pressure inside the vessels. Approximately 9 mL of metals grade HNO_3 and 1 mL of metals grade HCl was added to each vessel. The vessels were then weighed before the digestion. One set of samples was used as a blank B100 while the other sets were used for matrix spike (MS) recovery at five different concentrations (Appendix 1). For B100 spiked samples, a water-based spiking solution (Catalog No. MIXSTD1-5, Spex, Certiprep, USA) was added after the digestion process. The spiking solution contained multiple elements in different concentrations (Appendix 1). The blank B100 samples were used for MS recovery calculations. The purpose of these MS samples was to determine the effect of B100 on the final results at different concentrations and consequent instrument response. A separate concentration verification standards were prepared similarly. Another set of blank B100 samples and oil standards (Catalog No. S23-100Z, Spex, Certiprep, USA) were analyzed using ASTM standard method D4951-02 [9] where the solutions are introduced to the ICP by free aspiration.

2.3. Microwave Assisted Acid Digestion

Microwave Accelerated Reaction System (MARSXpress, CEM Corporation, Matthews, NC) was used to digest the acidified samples. The full power of the system was approximately 1200 W of microwave energy at a frequency of 2.45 GHz. The system was equipped with a 40-vessel turntable. The instrument was pre-calibrated according to manufacturer specifications. Method parameters of the microwave system were 600 W power (100%), ramped to

175 °C in 5.5 min, hold for 4.5 min, and then cool-down for 1 h.

2.4. Post-Digestion Samples Treatment

The samples were weighed after the digestion process to make sure the weight loss was less than 10% [14]. Approximately 20 mL of reagent grade deionized water (18 mΩ) was added to each vessel and then transferred to centrifuge tubes. The final volume was brought to 50 mL. A white turbid coloration was observed at this point due to alcohol formed as a result of ester hydrolysis. A clear solution was obtained by centrifugation at approximately 1000 rpm for five min. To be able to run through the ICP-OES by pneumatic nebulization, turbidity values less than 1 NTU (nephelometric turbidity unit) are preferred [15]. The digested solution was stable over considerable period of time without change in color, matrix, or concentration of most of the metals.

2.5. Instrument Setup and Calibration

All analyses in this study were performed using Varian Vista MPX simultaneous inductively coupled plasma optical emission spectrometer (ICP-OES) with axially viewed plasma. The instrument was equipped with a mass flow controller on the nebulizer gas and 3-channel peristaltic pump. The system was optimized for best performance. The instrument operation parameters are given in Table 1.

Table 1. Instrument Operating Conditions

Power	1.10 kW
Plasma gas supply:	Argon, ultra high pure (99.99%)
Plasma gas flow:	15.0 L/min
Auxiliary gas flow:	0.75 L/min
Nebulizer gas flow:	0.75 L/min
Nebulizer type:	SeaSpray/Ezyfit Glass Concentric (Glass Expansion, Melbourne, Australia).
Spray Chamber:	Cyclonic twister, Varian Inc.
Torch:	Axial, high-solids, Varian Inc.
Pump speed:	15 rpm
Sample Delay:	40 s
Rinse time:	15 s between each sample
Replicate read time:	15 s
Instrument stabilization delay:	10 s
Replicates:	3
Background correction:	Fitted
Correction type:	Point sum
Autosampler:	SPS-3, Varian Australia Pty Ltd

Since this method was an attempt to analyze biodiesel samples alongside other environmental samples, water-based multi-element calibration standard curves were prepared in 5% nitric acid and DI water using certified standard solutions (Spex Certiprep, Metuchen, NJ, USA). Most of the elements were analyzed at two or three different wavelengths

to differentiate the instrument response at lower or higher concentrations. A seven point calibration curve is was run using different concentrations for different elements based on the values normally expected in environmental matrices. Table 2 shows correlation coefficient values (R^2) and instrument detection limits as obtained for all the elements which were significant at values greater than 0.995.

2.6. Instrument Detection Limits (IDL)

The water-based IDLs were determined as three times the standard deviation (SD) of seven replicates of a concentration verification standard (Spex Certiprep, Metuchen, NJ, USA) at concentrations 3 – 5 times the manufacturer's IDL on three non-consecutive days [16]. The biodiesel-based IDLs were determined by digesting at least seven aliquots of B100 samples as mentioned above. A water-based spiking solution containing a concentration verification standard at concentrations 3 – 5 times the manufacturer's IDL were added before bringing the samples up to 50 mL final volume. IDLs were then calculated as 3xSD on three non-consecutive days.

2.7. Precision and Accuracy

Relative percent deviation (RSD) for replicate analyses of the same sample were obtained as $RSD = (\text{standard deviation}/\text{mean value}) \times 100$. The RSD values for replicate measurements of a sample were obtained from the Expert Software supplied with the ICP.

For matrix spike recovery, results for all the spiked samples were adjusted to exactly 0.5000 g of B100 and 50 mL post-digestion final volume. Recovery was then calculated as:

$\% \text{ Recovery} = (\text{conc. in spiked sample} - \text{conc. in unspiked sample}/\text{actual spike conc.}) \times 100$

Calculations: Final concentration of element in B100 samples was calculated as:

Concentration of element in B100 (mg/kg) = $\text{Conc. (mg/L)} \times \text{Vol. (L)}/W \text{ (kg)}$

where *Conc.* is the concentration of the element obtained by ICP in mg/L, *Vol.* is the final volume of the digested solution in liters, and *W* is the weight of the B100 sample in kg.

3. RESULTS AND DISCUSSION

The acceptable weight loss (<10% of the whole digestate including sample, HNO₃ and HCl solution mentioned in section 2.2, sample preparation) during sample digestion indicated that a microwave assisted acid digestion system equipped with a pressure release vent can be utilized for elemental analyses [14] of B100 biodiesel. The graph in Fig. (1) shows that reducing the sample weight from 0.5 g to 0.25 g reduces the weight lost during digestion process ($R^2 = 0.86$). The weight loss is affected by different factors including the amount of organic carbon present in the sample, pressure exerted on the vessel's vent, and torque applied to close the caps on digestion vessels. Therefore, a linear trend was not established while increasing the sample weight. Lower sample weight reduced the weight loss, however, minimum detectable concentrations of trace elements in final solutions or biodiesel would be affected. The digested samples were homogeneously diluted with

Table 3. Change in Signal-to-Background Ratios (SBR) of Selected Elements in a 5 mg/L Aqueous Standard; before and after Running B100 Spiked Samples

Element	Before	After	% Change	Element	Before	After	% Change
Al 236.705	2.308	2.534	10%	Mn 257.610	218.622	211.9465	-3%
Al 308.215	5.843	6.3525	9%	Mo 202.032	58.737	60.531	3%
Al 396.152	9.817	10.7445	9%	Ni 230.299	26.602	27.187	2%
As 188.980	12.463	13.2065	6%	Ni 231.604	32.299	32.777	1%
As 193.696	9.043	9.7505	8%	Pb 220.353	13.759	14.339	4%
As 234.984	2.046	2.2235	9%	Pb 283.305	1.73	1.8775	9%
Ba 455.403	117.967	122.392	4%	S 181.972	0.171	0.1705	0%
Cd 214.439	156.706	159.904	2%	S 182.562	0.017	0.017	0%
Cd 226.502	108.162	108.974	1%	Sb 206.834	0.134	0.1425	6%
Co 228.615	51.945	53.2045	2%	Se 196.026	6.428	6.9445	8%
Co 238.892	41.616	45.7495	10%	Sr 407.771	260.321	295.093	13%
Cr 267.716	61.651	62.986	2%	Th 288.505	0.091	0.0875	-4%
Cu 324.754	26.774	29.1675	9%	Tl 337.280	0.008	0.008	0%
Cu 327.395	18.531	20.8925	13%	Zn 202.548	112.015	113.314	1%
K 766.491	42.721	41.6565	-2%	Zn 206.200	45.036	44.53	-1%
K 769.897	37.214	37.3615	0%	Zn 213.857	124.548	117.2985	-6%

introduction system for one environmental matrix without compromising the sensitivity for others.

The instrument detection limits for water-based samples was one to several fold lower than those determined using blank B100-based samples (Appendix 1). Elements like Ca, Mg, P, and S, were present at trace concentration as contaminants in biodiesel samples. The catalyst used in the production process, K or Na, has lower IDLs in biodiesel-based samples. Overall, the IDLs indicated that the method can be used to detect concentrations significantly lower than those specified under ASTM 6751 for B100 biodiesel. For potassium determination, wavelength line K 769.897 nm has better detection and sensitivity at lower or higher levels compared to K 766.491 nm. No significant interference was observed except the matrix background concentrations. Based on the IDLs, the minimum detectable concentration (MDC) of K in biodiesel is approximately 3 mg/L for a final digestate volume of 50 mL. However, lowering the final digestate volume lowers the MDC; for instance, 1.5 mg/L in 25 mL. Lower levels are possible through further concentrating the digestate. The term MDC mentioned here is the calculated final concentration of an element in the matrix, i.e. biodiesel, as determined by digesting a small sample aliquot diluted to a definite digestate volume for running through ICP-OES. Hence, examining MDCs and IDLs are helpful in determining the final digestate volumes. Currently, the ASTM and European Union standards [7, 8] for Na and K combined, is 5 mg/L. This was achieved by using K 766.491 together with Na 588.995 nm line. The Na 588.995 nm line has a lower MDC of approximately 2 mg/L compared to other Na lines (Na 589.592 nm and Na 568.821

nm with MDCs as 4 and 36 mg/L, respectively). Resolution and intensity for Na 568.821 nm line was low. Similarly, the EN 14214 standard for Ca and Mg combined is 5 mg/L. Fuel injection equipment manufacturers have proposed to limit the content of Na+K and Ca+Mg to 5 mg/L each [18]. Ca was noted for high background concentrations. We used two lines for Ca: Ca 317.933 nm and Ca 396.847 nm. The latter was found suitable for low values and high intensity. Approximately similar IDLs were obtained for the lines, however, Ca 317.933 nm was found more sensitive to higher concentrations. The study suggested suitability of Ca 396.933 nm for biodiesel analyses. The MDC for this line was approximately 3 mg/L based on the final volume of 50 mL which can be reduced by lowering the final volume. Mg 279.078 nm line was found to be sensitive compared to Mg 280.270 nm. Both have approximately 2 mg/L MDCs. The Ca+Mg combined 5 mg/L standard is hence achievable.

Phosphorus concentration was easily detectable at significantly lower levels. Two lines, P 213.618 nm and P 214.914 nm, were used in the current study. Both lines were sensitive to lower and higher concentrations. The IDLs were 0.002 and 0.005 mg/L with MDCs as 0.2 and 0.5 mg/L, respectively. Mo 213.606 nm has an insignificant interference with P 213.618 nm, while no interference was observed for P 214.914. The ASTM standard for P in B100 is 0.001% by mass, i.e., 10 mg/L (ASTM D6751).

Because of environmental consequences, the ASTM standard for sulfur content in fuel is reduced to 15 mg/L (ASTM D6751). This standard is easily determined by the current procedure. Two lines, S 181.972 nm and S 182.562 nm, were used. Both were sensitive to low and high

recommended. The sample size can be more precisely calculated from IDLs, MDCs, and the final volume of the digestate solution. This calculation should be based on an element of concern expected to be present in the lowest concentration while selecting a wavelength line more sensitive to trace levels. Another way to reduce the weight lost during the digestion process is sample pretreatment. Before digesting the sample in a microwave reaction system, the sample can be predigested in a hood for at least 15 minutes until the reaction stops.

Accuracy of the method determined by matrix spike recovery indicated sustained concentrations of the elements in the digested B100 samples. The study shows that the biodiesel matrix has no effect on the performance of the overall analyses and vice versa. There is no reference metal standard available in a FAMES-base (biodiesel-base) to further evaluate the method. Therefore, the aqueous standards were added after the digestion process to obtain B100 matrix spiked samples. The samples were hence

treated as environmental samples of sufficient organic loading. Significant correlation coefficient values observed by the spiked samples indicated that aqueous standard calibration curves are sufficient to analyze both water and digested B100 samples.

4. CONCLUSION

The current study revealed that the same instrumental conditions are sufficient to analyze aqueous samples concurrently with biodiesel (B100) samples without compromising the performance of the instrument or overall analysis. The method, therefore, help save time and cost associated with additional accessories and facilitating quick turnaround. The study shows that microwave assisted acid digestion can be employed to prepare biodiesel samples for metals analysis using ICP-OES. Biodiesel and its analysis are gaining significant potential especially for analytical community. This study, hence, proves an important addition to understand the analytical aspects of biodiesel B100.

APPENDIX 1

Biodiesel-Based (B100); Instrument Detection Limits (IDLs); Matrix Spike (MS) Concentrations and Recovery; and Relative Standard Deviation (RSD) Values

Element	IDLs Biodiesel Based, ppb	R ² , B100	Conc. in B100, ppm	MS#1 Conc. ppm	MS Recovery	RSD Replicate Analyses	Average RSD Off-Instrument	MS#2 conc. ppm	MS Recovery	RSD Replicate analyses	Average RSD off-Instrument	MS#3 conc. ppm	MS Recovery	RSD Replicate Analyses	Average RSD off-Instrument	MS#4 conc. ppm	MS Recovery	RSD Replicate Analyses	Average RSD off-Instrument	MS#5 conc. ppm	MS Recovery	RSD Replicate Analyses	Average RSD Off-Instrument
Ag 328.068	4.9	0.9368	0.0134	0.008	120.0%	19.1	7.1	0.16	107.6%	3.7	1.1	0.32	96.8%	16.8	1.5	0.4	84.2%	14.9	1.4	0.5	96.5%	-6.2	9.7
Al 236.705	17.1	0.9926	0.2429	0.036	144.7%	92.2	1.2	0.36	80.7%	6.5	1.8	0.72	69.3%	2.8	2.2	1.8	77.5%	1.3	0.9	5.0	91.8%	3.9	1.3
Al 396.152	6.8	0.9946	0.3016	0.036	132.3%	106.5	0.7	0.36	83.6%	8.3	1.1	0.72	71.3%	1.4	1.5	1.8	78.4%	0.5	1.0	5.0	88.0%	4.2	1.8
As 188.980	5.7	0.9948	0.0041	0.036	97.0%	8.2	5.5	0.36	106.8%	3.1	2.3	0.72	95.0%	2.6	1.2	1.8	100.7%	1.7	1.4	5.0	111.4%	1.5	1.4
As 234.984	18.2	0.9945	0.0546	0.036	106.5%	24.4	7.5	0.36	105.0%	3.0	2.6	0.72	91.7%	1.7	1.7	1.8	97.6%	1.5	1.4	5.0	109.9%	1.2	1.7
Be 313.042	0.1	0.9980	0.0007	0.008	103.6%	7.9	1.2	0.08	110.5%	2.5	1.1	0.16	98.8%	1.7	2.2	0.4	102.3%	1.1	1.9	1.0	91.5%	-	-
Ca 396.847	34.2	0.9848	1.402	0.800	103.2%	20.0	1.1	8.00	143.9%	2.4	1.6	16.00	118.0%	1.3	1.4	40.0	98.3%	1.3	0.9	100.0	60.9%	-10.3	1.0
Cd 226.502	1.1	0.9976	0.0022	0.036	103.4%	7.3	0.9	0.36	103.7%	4.5	0.8	0.72	92.0%	1.7	2.3	1.8	95.8%	1.0	1.3	5.0	102.9%	1.7	1.6
Co 228.615	1.2	0.9982	0.0026	0.036	103.0%	8.0	1.6	0.36	104.6%	4.4	0.8	0.72	92.6%	1.2	1.1	1.8	95.3%	0.9	1.2	5.0	101.9%	2.0	1.7
Co 238.892	2.0	0.9974	0.0025	0.036	104.0%	8.8	1.9	0.36	103.2%	4.2	0.7	0.72	91.1%	1.8	2.1	1.8	93.7%	1.3	1.2	5.0	98.9%	1.9	1.3
Cr 267.716	1.4	0.9978	0.0049	0.036	99.4%	1.7	1.0	0.36	106.1%	4.3	0.7	0.72	94.2%	1.2	1.3	1.8	96.6%	1.1	1.4	5.0	104.4%	1.7	1.7
Cu 324.754	1.9	0.9973	0.0069	0.036	105.2%	10.0	1.4	0.36	107.4%	4.1	0.8	0.72	94.1%	1.0	1.2	1.8	97.0%	1.2	1.1	5.0	105.7%	1.9	1.7
Cu 327.395	2.3	0.9974	0.0026	0.036	104.3%	8.5	1.6	0.36	107.5%	4.3	0.9	0.72	94.3%	1.0	1.3	1.8	97.6%	0.9	1.4	5.0	106.1%	1.8	1.7
Fe 238.204	24.0	0.9954	0.1715	0.800	103.1%	7.2	0.9	8.00	115.6%	2.7	1.4	16.00	101.2%	0.2	0.8	40.0	101.9%	0.5	1.9	100.0	86.7%	-18.4	2.9
Fe 259.940	16.1	0.9954	0.1833	0.800	103.5%	7.5	1.1	8.00	116.0%	2.7	1.4	16.00	102.0%	1.2	2.1	40.0	101.8%	0.4	1.9	100.0	86.7%	-16.7	2.7
K 766.491	37.7	0.9922	ND	1.080	107.8%	8.4	2.0	10.80	94.3%	2.7	2.0	21.60	86.8%	3.2	0.9	54.0	92.1%	1.0	1.8	100.0	110.1%	2.9	0.8
K 769.897	32.7	0.9853	ND	1.080	104.9%	4.5	2.3	10.80	86.3%	2.3	1.6	21.60	81.6%	3.2	1.1	54.0	92.3%	1.2	1.9	100.0	119.5%	3.1	0.8
Mg 279.078	16.1	0.9984	0.1309	0.800	103.9%	7.9	0.7	8.00	110.2%	4.3	0.5	16.00	98.1%	1.4	1.3	40.0	102.8%	1.0	1.4	100.0	93.3%	0.0	21.8
Mg 279.553	21.3	0.9767	0.6765	0.800	105.6%	12.4	1.1	8.00	156.1%	1.9	1.7	16.00	127.5%	0.9	1.4	40.0	100.3%	0.5	1.6	100.0	55.2%	0.0	9.7
Mg 280.270	22.2	0.9982	0.3522	0.800	104.0%	9.3	1.4	8.00	132.0%	3.1	1.7	16.00	114.1%	0.5	0.9	40.0	101.7%	2.0	1.2	100.0	68.8%	0.0	5.6
Mn 257.610	1.1	0.9987	0.0049	0.036	103.6%	7.7	1.0	0.36	108.7%	2.5	1.3	0.72	95.2%	1.7	2.1	1.8	95.8%	0.4	1.7	5.0	101.5%	2.1	1.0
Mo 202.032	135.7	0.9983	ND	0.036	103.3%	4.1	0.8	0.36	109.1%	3.6	1.8	0.72	95.9%	1.1	1.2	1.8	99.4%	0.7	1.2	5.0	106.2%	1.6	1.7
Na 568.821	364.5	0.9925	0.7916	0.800	113.3%	11.5	12.3	8.00	113.8%	4.1	1.7	16.00	97.9%	3.8	1.3	40.0	101.3%	0.3	1.4	100.0	75.6%	-22.1	39.1
Na 588.995	18.3	0.9670	1.1995	0.800	113.5%	18.3	1.3	8.00	134.1%	4.0	2.2	16.00	112.3%	2.4	0.8	40.0	99.9%	1.6	1.0	100.0	64.1%	-29.2	1.1
Na 589.592	34.5	0.9780	0.8112	0.800	111.1%	16.8	2.1	8.00	120.2%	4.0	2.2	16.00	105.8%	2.6	0.9	40.0	101.1%	1.6	1.2	100.0	67.8%	-45.6	1.6
Ni 230.299	1.4	0.9982	0.0031	0.036	101.4%	4.8	1.1	0.36	105.5%	4.2	0.8	0.72	93.2%	1.5	1.2	1.8	94.8%	0.7	1.0	5.0	100.9%	1.7	1.5
Ni 231.604	1.2	0.9983	0.0041	0.036	101.5%	4.0	0.8	0.36	104.8%	3.2	1.8	0.72	92.1%	1.4	1.2	1.8	94.7%	1.1	1.0	5.0	100.7%	1.7	1.6
P 213.618	1.9	0.9960	0.0042	0.080	102.2%	6.5	0.6	0.80	106.1%	4.5	0.6	1.60	95.9%	1.1	1.5	4.0	102.5%	1.1	1.1	-	-	-	-
P 214.914	4.5	0.9955	0.0012	0.080	102.6%	6.6	2.2	0.80	108.4%	3.2	1.8	1.60	96.7%	2.8	1.1	4.0	102.7%	1.3	1.4	-	-	-	-
Pb 220.353	1.6	0.9984	0.0027	0.036	105.7%	8.0	3.5	0.36	96.3%	3.3	2.0	0.72	85.2%	2.3	1.1	1.8	94.2%	0.7	1.3	5.0	99.9%	1.6	1.6
S 181.972	5.5	0.9964	0.0491	0.080	106.7%	17.8	0.9	0.80	104.8%	2.9	1.8	1.60	95.0%	3.2	1.2	4.0	101.2%	1.1	1.4	-	-	-	-
S 182.562	5.9	0.9964	0.0098	0.080	108.2%	16.9	7.8	0.80	104.6%	3.2	2.3	1.60	94.9%	2.9	1.1	4.0	102.2%	1.2	1.3	-	-	-	-
Sb 206.834	6.2	0.9988	0.0030	0.008	96.5%	15.7	13.6	0.08	105.9%	4.2	3.4	0.16	95.1%	2.4	2.6	0.4	102.3%	1.4	1.8	1.0	95.2%	4.0	2.7
Se 196.026	30.1	0.9924	0.0380	0.036	93.1%	22.2	4.6	0.36	111.3%	3.6	2.3	0.72	98.3%	3.2	1.2	1.8	105.6%	2.1	1.8	5.0	116.0%	1.3	1.4
Si 251.611	27.0	0.9934	0.0404	0.080	106.1%	10.2	1.1	0.80	111.8%	1.5	1.4	1.60	96.4%	1.4	1.1	4.0	102.2%	2.1	0.9	-	-	-	-
Sn 189.927	2.3	0.9897	0.0080	0.004	119.5%	26.6	10.6	0.04	121.4%	4.7	3.6	0.08	110.7%	2.6	1.4	0.2	98.8%	2.5	2.0	-	-	-	-
Sr 407.771	23.2	0.8868	0.3892	0.828	104.2%	10.4	1.0	8.28	115.2%	2.9	1.4	16.56	91.1%	1.4	1.3	41.4	69.4%	1.0	0.8	105.0	38.7%	1.6	0.9
Th 288.505	3.6	0.9982	0.0072	0.008	94.8%	7.9	15.7	0.08	104.3%	2.4	3.1	0.16	94.7%	2.2	1.5	0.4	100.9%	0.5	2.1	1.0	90.9%	1.3	2.9
Tl 190.794	5.8	0.9978	ND	0.008	70.9%	7.7	36.7	0.08	0.0%	4.7	2.2	0.16	0.0%	2.0	1.8	0.4	103.1%	2.1	0.9	1.0	93.5%	1.0	6.9
V 292.401	0.9	0.9970	0.001	0.008	101.8%	8.6	3.5	0.08	111.6%	3.5	1.8	0.16	98.8%	1.0	1.3	0.4	102.3%	1.0	1.1	1.0	89.4%	-	48.3
Y 360.074	2.1	0.9992	ND	0.080	103.9%	8.8	0.9	0.80	111.9%	2.8	1.4	1.60	98.2%	1.5	2.1	4.0	101.8%	0.7	2.1	-	-	-	-
Y 371.029	2.2	0.9987	ND	0.080	104.2%	8.9	1.2	0.80	113.1%	2.9	1.4	1.60	99.4%	1.4	2.1	4.0	102.4%	1.4	1.3	-	-	-	-
Zn 202.548	0.7	0.9978	0.0089	0.036	108.8%	12.4	0.8	0.36	103.0%	5.1	0.9	0.72	94.9%	4.0	1.5	1.8	96.0%	0.7	1.2	5.0	103.3%	1.8	1.5
Zn 206.200	1.3	0.9979	0.0085	0.036	108.3%	11.5	1.8	0.36	102.9%	3.7	2.1	0.72	94.5%	3.0	1.1	1.8	95.9%	1.0	1.1	5.0	103.1%	1.6	1.7
Zn 213.857	0.9	0.9951	0.0069	0.036	108.3%	12.2	0.7	0.36	99.4%	4.0	0.6	0.72	91.3%	3.5	1.3	1.8	93.6%	1.1	1.5	5.0	103.8%	1.9	1.6

Abbreviations used: ppm - parts per million (mg/L); ppb – parts per billion (µg/L).

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