

Tungsten coil atomic emission spectrometry: calcium determination in biodiesel samples

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In this application note, tungsten coil atomic emission spectrometry was used for direct determination of Ca in biodiesel samples. Discrete volumes of biodiesel (10 µL) were directly placed on the tungsten coil with a micropipette and an appropriated heating program was applied to decompose the samples. The first four heating steps (0.32; 0.35; 0.36 and 0.37 V for 20; 50; 50 and 50 s, respectively) were employed to dry the sample and decompose organic matrix. The purge gas flow rate, composed by a mixture of 90 % v/v plus 10 % v/v hydrogen, was stopped during the drying/matrix decomposition steps to minimize temperature gradients in the sample drop in contact with the hot metallic surface. The analytical figures of merit for Ca (emission wavelength = 422.7 nm) were determined with calcium reference solutions. Two different linear ranges were observed, 0.2 – 1.0 and 1.0 – 10.0 mg L⁻¹. The detection limit (LOD) was estimated as 0.15 mg L⁻¹, which corresponds to 0.17 mg kg⁻¹ in biodiesel, and the relative standard deviation (n = 10, 2 mg L⁻¹ Ca) was estimated as 2.6 %. Sample throughput was approximately 20 samples h⁻¹. The accuracy was proved by an addition-recovery experiment.

Keywords: calcium, biodiesel, tungsten coil, *in situ* digestion

Techniques: Tungsten coil atomic emission spectrometry, WCAES

Applications: Feasibility testing, Quality control, Process monitoring

Background

Tungsten has been successfully employed as an atomizer and vaporizer in electrothermal atomic spectrometric methods. Tungsten coil extracted from light bulbs were employed as atomizers for atomic absorption, emission and fluorescence spectrometry measurements. Simultaneous determination by atomic emission lines employing a multi-channel system detector (charge coupled device, CCD) was reported by the first time in 2005, and this method was called tungsten coil atomic emission spectrometry (WCAES). Some favorable characteristic are associated with WCAES in comparison to traditional methods, such as portability, low cost, multi-element capacity and small sample volume requirements. Usually acid aqueous solutions containing the samples are directly introduced into the coil, however slurries sampling has also been successively attempted. The typical lifetime of a tungsten coil may vary from 150 to 500 runs without any surface chemical treatment, though; this parameter is extremely dependent upon the purity and composition of the purge gas and the sample matrix.

Biodiesel is a renewable fuel for diesel engines and may be used as an alternative to the use of diesel oil derived from petroleum. Throughout biodiesel production, vegetable or animal oils are converted in methyl or ethyl esters, after transesterification reaction, with an alcohol (methanol or ethanol) in presence of a catalyst, the reaction yields glycerol as a co-product, and this compound is usually removed after successively washing steps. During the purification step, some metals may be introduced into biodiesel depending on water composition and drying agents, such as calcium oxide and magnesium sulfate. Calcium and Mg may cause the formation of insoluble soap in biodiesel and its use giving rise to incrustations causing damage of engine. There is no specific legislation targeting Ca alone, but maximum levels tolerated for Ca plus Mg in biodiesel are 5 mg kg⁻¹ according to Brazilian, European Community and the the United States legislations.

In this application note, a direct *in situ* procedure for Ca determination in biodiesel was developed using a labmade WCAES. The heating program was optimized aiming *in situ* decomposition of the biodiesel samples and calibration with aqueous solution without addition of any chemical reagent.

Measurement conditions

The WCAES device (Figure 1) consists of a commercial tungsten coil (Osram, Pullach, Germany) used as atomizer and excitation source for calcium. The coil was housed into a borosilicate glass cell, equipped with quartz windows on either sides and connected to two copper electrodes.

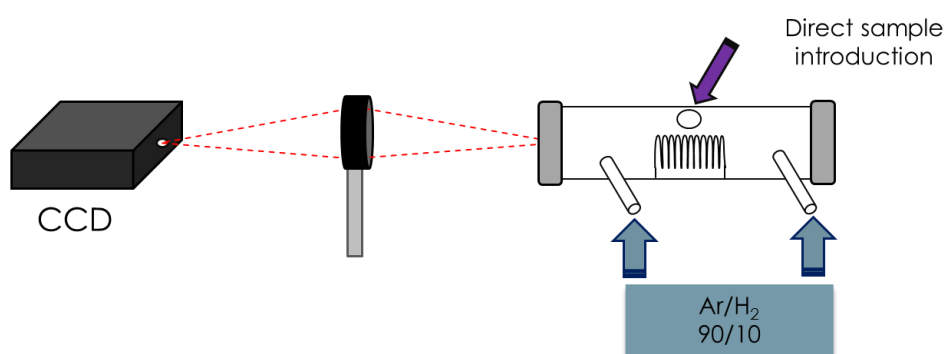


Figure 1 – Schematic diagram of the WCAES instrumental setup.

The cell contains a port to sample introduction and escape of the gases and inlets for introducing the gas mixture of H₂/Ar (10 and 90 % v/v respectively, flowing at 1.0 L min⁻¹), used to prevent coil oxidation and to cool down the atomizer after the atomization step. A volume of 10 µL of the biodiesel sample or Ca reference solutions was directly inserted on the tungsten coil, with the aid of mechanical micropipette (Eppendorf 10-100 µl, Brinkman, Westbury, NY, USA). A heating program (Table 1), including drying, pyrolysis and atomization steps was used for analytical calibration solutions prepared in aqueous medium.

Table 1 – Tungsten coil heating program for aqueous solutions

Step	V applied (V)	Time (s)
1	0.70	30
2	0.65	10
3	0.60	10
4	0.50	10
5	0.40	10
6	0.30	10
7	1.0	5
8	14.0	3

For biodiesel samples, the heating program (Table 2) was optimized in order to avoid sample losses due to overheating the coil during the dry steps. The atomic emission signal was collected by a fused silica lens and focused as a 1:1 image onto the entrance slit of a CCD spectrometer (Ocean Optics, HR 4000, Dunedin, FL, USA). The spectrometer was fitted with a 50 μm entrance slit and 3648 pixels, providing a spectral window of approximately 100 nm. All measurements were carried out in triplicate and emission data were obtained from peak area of the Ca emission signal at 422.7 nm using the Spectrometer Operating Software (OOIBase32, Ocean Optics). For background (BG) correction, the near background line in the spectra immediately before and after Ca emission signal was used, for this, three different channels were used for the simultaneous acquisitions signals, the first for Ca emission in 422.7 nm and the others for background signals acquisitions. Background correction was achieved mathematically subtracting the BG signal from the Ca emission signals using the data acquisition and control software.

Table 2 – Tungsten coil heating program for biodiesel samples

Step	V applied (V)	Time (s)	Ar/H ₂
1	0.32	20	Off
2	0.35	50	Off
3	0.36	50	Off
4	0.37	50	Off
5	0	5	On
6	1.0	10	On
7	0	5	On
8	14.0	3	On

Results

The heating program for biodiesel samples (Table 2) was optimized to promote the matrix decomposition and prevent sample outflow and splashing. The optimization was carried out employing 10 μ L of biodiesel. The first four heating steps (0.32, 0.35, 0.36 and 0.37 V for 20, 50, 50 and 50 s, respectively) were implemented to dry the sample and decompose the organic matrix. The gradual and lower increase of the output voltage prevent outflow sample due to overheating of the coil. To minimize temperature gradients among parts of the sample in contact with the hot metallic surface or with the gas flow at room temperature, the purge gas flow rate was stopped during these matrix decomposition/drying steps. This prevented sample splashing and contributed to improving repeatability and accuracy. In the next step, the purge gas flow rate was reestablished to remove the smoke generated and 1.0 V was applied for 10 s to pyrolyze the sample. Finally, a 14.0 V, 5 s atomization step was applied for atomizing and exciting Ca and generating emission signals. Using this heating program, more than 50 heating cycles for biodiesel samples were performed with only one tungsten coil. During the optimization of the procedure for Ca determination in biodiesel samples, it was observed that successive measurements of a

solution containing 2.0 mg L^{-1} of Ca presented a relatively high relative standard deviation (RSD) value when using peak height measurements and an integration time of 200 ms, i.e. RSD was 13.8 % for 10 measurements Figure 2 shows ten successive emission signals for Ca at 422.7 nm.

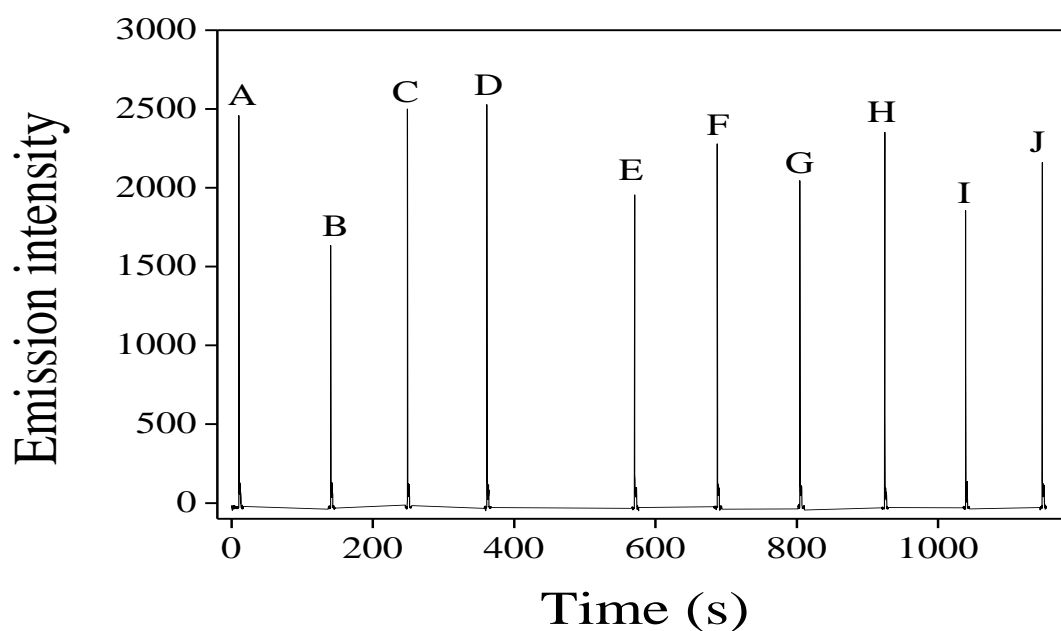


Figure 2 – Ten successive emission signals for 2.0 mg L^{-1} Ca at 422.7 nm.

Although peak height does depend on the analyte concentration in the sample, it is also affected by other factors, such as atomization and excitation rate and the flow rate of the purge gas. Cloud atoms are formed in the tungsten coil and diffuse out of it by expansion and the flow of the protection gas, consequently the emission intensity rises and falls in a peak-shaped signal, forming a transient signal. Peak height is a measurement of the maximum population of excited atoms which occurred in the tungsten coil during atomization. If some factors such as the heating rate of the tungsten coil during the atomization step affect the rate of atoms formation, the maximum excited atoms population and the peak height are also affected, as shown in Figure 3 for the first three transient signals for a 2.0 mg L^{-1} Ca solution. However, satisfactory results was obtained using peak area ($\text{RSD} = 2.6 \%$, $n = 10$) since integrated peak

area measurements are independent on the atomization rate. Thus, all further measurements were based on peak area. Peak area measurements are not usually used with tungsten coil atomizer, but they may be needed here probably due to effects of the biodiesel matrix on the tungsten coil surface and consequently on the atomization mechanism.

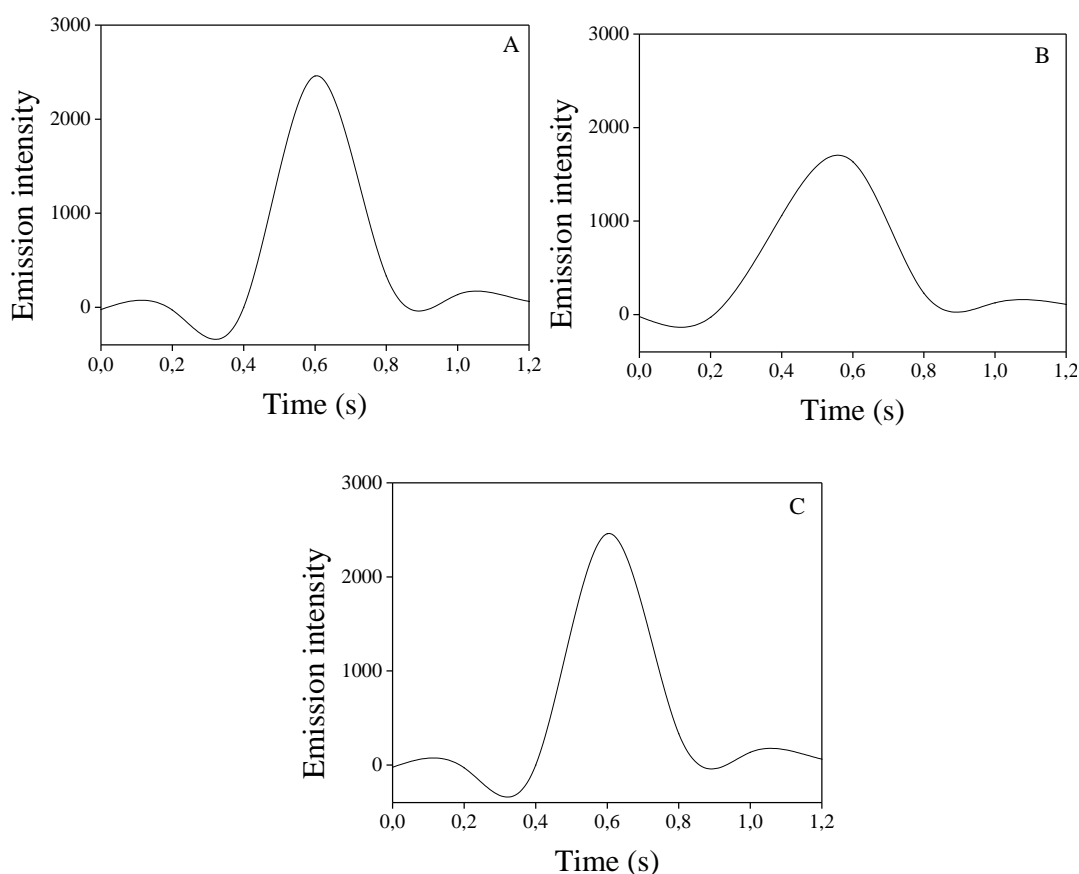


Figure 3 – Transient signals for 2.0 mg L^{-1} Ca (422.7 nm). Transient signals for the first (A); second (B) and third (C) peaks presented in Figure 2.

The analytical figures of merit for Ca were determined using the heating program presented in the Table 1 for aqueous reference solutions. Two different linear ranges were observed, $0.2 - 1.0$ and $1.0 - 10.0 \text{ mg L}^{-1}$, which presented the following calibration curve equations: $S = 292.02C + 12.58$ ($r = 0.995$) and $S = 85.01C + 67.01$ ($r = 0.993$), respectively. In this case, S represents the analytical signal based on peak area and C is the Ca concentration in mg L^{-1} . The detection limit (LOD) was estimated as 0.15 mg L^{-1} , which

corresponds to 0.17 mg kg⁻¹ in biodiesel, and the relative standard deviation (n = 10, 2 mg L⁻¹ Ca) was estimated as 2.6 %. Sample throughput was approximately 20 samples h⁻¹.

Three biodiesel samples were analyzed to check the applicability of the proposed procedure, the heating program presented in Table 2 was used for Ca determination after *in situ* decomposition and vaporization. Analytical calibration curves were built employing aqueous solution and the heating program presented in the Table 1. Recoveries for the three samples spiked with 2.0 or 4.0 mg kg⁻¹ are shown in Table 3, with recovered values in the range of 91.6 – 106.7%, indicating the absence of matrix effects in Ca determination. All analyzed samples contained Ca in concentrations lower than the detection limit.

Table 3 – Addition and recovery for Ca determination in biodiesel samples

Sample	Added (mg kg ⁻¹)	Found (mg kg ⁻¹)	Recovered (%)
	0	< 0.17	-
Biodiesel 1	2.0	1.92	95.5
	4.0	4.27	106.7
	0	< 0.17	-
Biodiesel 1	2.0	2.24	112.1
	4.0	3.66	91.6
	0	< 0.17	-
Biodiesel 1	2.0	1.92	95.6
	4.0	4.03	100.6

Conclusions

The developed procedure for Ca determination in biodiesel sample employing *in situ* digestion is a good alternative to the ICP OES method established in the Brazilian, the USA and European Community regulations. Some advantages that should be emphasized are the calibration using reference solutions prepared in aqueous medium, the short time of *in situ*

digestion (*ca.* 3 min) and no need of using an organic solvent for sample dilution or preparation of solutions for calibrations. Addition-recovery experiments showed that the WCAES procedure presented proper accuracy and precision. Moreover, measurements based on peak area provide better repeatability in comparison to peak height.

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