DETERMINING PPM CONTENTS OF COPPER AND ZINC IN BIODIESEL WITH ENERGY-DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY

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Energy-Dispersive X-Ray Fluorescence spectrometry was used for determining ppm contents of copper in biodiesel, as a tool for evaluating the aggressiveness of biodiesel to copper alloys. As the copper peaks were very small (from around 500 to around 2000 counts, for 10-minute measurements with reference samples), the determination of their areas, made with the PyMCA software, had to be extremely careful. Two spectrometers were compared. Both use Si-drift detectors. One of them uses an Ital-Structures W-tube, while the other uses two Oxford tubes, one with Cr anode and the other with W anode. For Cr-tube, a PMMA filter was used. As a linear correlation can be found between the Cu-K areas and the Cu content in the biodiesel, calibration biodiesel samples were prepared by adding controlled amounts of copper. Two addition methods are compared. When applied to biodiesel samples obtained from corrosion weight-loss tests, he obtained Cu contents were sensitive to the corrosion test variables, and were coherent with the weight-loss results.

1. Introduction

The quantification of metallic ions in liquids may be used as a measure of the corrosion kinectics of metals and alloys immersed in these liquids, as a complement of weight loss measurements. As copper and copper alloys are prone to be corroded in biodiesel [1,2], special attention is being directed in our group to the analysis of this corrosion process [3]. The present work discusses the analysis by Energy-Dispersive X Ray Fluorescence spectroscopy (EDXRF) of copper and zinc ions in biodiesel which had been in contact with copper and brass samples during weight loss measurements according to ASTM G31 standard [4]. In EDXRF, no absorption and enhancement effects should be expected for systems where the analyte is a very much diluted species in a light matrix, and, therefore, a linear correlation should be expected between peak areas and content. So, EDXRF may be an adequate tool for quick quantitative analysis of these systems. The present work focuses in three important questions for these analyses − calibration, sensibility and reproducibility −, and compares different methods and experimental setups.

2. Methods

2.1 EDXRF

Two spectrometers, described in Table I as "A" and "B", respectively, were used in this work. Spectrometer A uses a water-cooled ItalStructures W-tube and a Ketek Si-drift x ray detector supplied in 2004. Spectrometer B uses two air-cooled Oxford XTF5011 tubes (W and Cr-anodes, respectively) and a recent Amptek Si-drift detector, supllied in 2011. For some experiments, detectors were interchanged.

Table I – EDXRF spectrometers used in the work

	X ray tube (lateral window)							X ray detector (Si-drift)				
	anode	max kV/mA	cooling	collimator (mat., Ø)	Be µm	angle to surface	filter	Be window	collimator	Si area /thickness	distance to sample	angle to surface
A	W	60/1.5	water	Pb, 1.3mm		45°		8 µm	Zr	5mm^2/450 µm	7 mm	45°
B	W	50/1	air	Ta, 1.3mm	125	63°		12.5 µm	multilayer	6 mm^2/500µm	10 mm	90°
	Cr	50/1	air	Ta, 1.3mm	125	63°	PMMA					

Most measurements with spectrometer A were done with 55keV and 1.1mA, for 1000s live time. Most measurements with spectrometer B were done with 50keV, .2mA and 1000s live time. The areas of the peaks were determined by PyMCA software [5].

2.2 Biodiesel preparation and exposition to copper and bronze

For the experiments on sensibility and reproducibility, biodiesel was prepared from soya oil by transesterification with ethanol. For the corrosion tests, commercial B100 biodiesel was used. Immersion tests according to ASTM G31 standard were carried out to evaluate the influence of the temperature and air bubbling in the corrosion rate of brass and copper. The metallic samples were displayed in three different levels, where two metallic samples remained totally immersed in the biodiesel, two others partially immersed and the last two ones exposed to biodiesel vapors. Air bubbling was provided by glass tubes with glass frits. After exposition, the metallic samples were weighted and the biodiesel was analyzed by EDXRF.

2.3 Preparation of biodiesel samples for calibration

Controlled amounts of copper were added to non-exposed biodiesel in order to generate calibration samples. As copper compounds are almost insoluble in biodiesel, they were first solved in methanol, which was then emulsified in biodiesel. $CuSO_4.5H_2O$ was used as the copper source, and samples with 1, 5, 10, 30 and 50 ppm Cu were prepared, through the mixing of 5% Cu-containing methanol and 95% biodiesel. As stable methanol-in-biodiesel emulsions are difficult to obtain, two different strategies were tried to ensure a homogeneous distribution of the Cu/Co carrying-methanol in the biodiesel reference samples during the essays. The first one was to promote vigorous stirring just before the essays. This method will be referred to as "full emulsion" along the text. The second one was to allow virtually all the methanol to evaporate before the essays, by heating the mixture at 70°C during the stirring process, for 10 minutes. In this second strategy, some biodiesel was also evaporated, as illustrated in Figure 1, and this amount was taken into account in the concentration calculations, assuming the final weight to correspond only to biodiesel. This method will be referred to as "methanol-evaporation" along the text.

3. Results

3.1 Typical spectra

Figure 2 presents a typical spectrum of biodiesel with 25ppm-added copper in spectrometer A. One observes that the strongest peaks correspond to Zr, at 15.77 and 17,67keV. Zr is present in the collimator of the Ketek detector, and is excited by the incoming x ray beam. The Cu-K peaks are in the "valley" of the spectrum and are shown with more detail in the inset. One observes that both Cu-K peaks are overlapped with Hf-L peaks. Cu-KL3 (8.05keV) overlaps with Hf-L3M4 (7.9keV), while Cu-KM3 (8.90keV) overlaps with Hf-L2M4 (9.02keV). Hf

peaks probably comes also from the detector collimator, as Hf is a usual contamination of Zr. A small Zn-K peak (KL3 = 8.64 keV) was also observed. It was attributed to the biodiesel sample holder.

Figure 3 presents a typical spectrum of biodiesel with 25ppm-added copper in spectrometer B, with Cr-tube and PMMA filter. Besides the Cu-K peaks, one observes Ar-K (2.96 and 3.19keV), Cr-K (5.41 and 5.95keV), escape-Ni-KL3 (5.74keV) and Ni-K (7.48 and 8.26keV). The last one, Ni-KM3, is partially overlapped with Cu-KL3 (8.05 keV). Ni, as already mentioned, comes from the biodiesel sample holder. It is only detected with the Amptek detector. The Ketek detector has a less wide detecting angle and does not receive these lateral x rays.

3.1 Peaks originated from the x ray tube anode material

W-tubes energy profiles are in principle more adequate for exciting Cu-K than those of Cr-tubes, because they present a higher intensity in the energy range above the Cu-K absorption edge. However, W-L peaks from the scattered incident beam will be very close to Cu-K peaks, thus impairing the determination of their areas. It was observed that the intensity of these W peaks depends both on the model of the W-tube and on the detector model, as can be seen in Table II. The different behavior of the two W-tubes should be ascribed mainly to their internal geometry, electron beam energy profile and Be-window thickness. The different behavior of the two detectors, on the other side, should be ascribed mainly to their different detection angle, which is much wider in the Amptek detector.

Table II - Area of W-L peaks for analysis of W-free oil with W-tubes (1000s live time)

detector	Amptek	Amptek	Ketek	Ketek
tube	Oxford	ItalStructures	Oxford	ItalStructures
operation	50kV /0.03mA	55kV/0.03mA	50kV /0.08mA	55kV/0.08mA
area (counts)	$2.4 \cdot 10^6$	$0.5 \cdot 10^3$	$2,1 \cdot 10^4$	not detected

On the other side, Cr peaks originated from Cr-tubes are not harmful to the determination of Cu-K peak areas. However, it was observed that the intensity of these peaks in our systems is very high, thus requiring a low photon flux to be used in order not to saturate the detector. Using a 4mm-PMMA filter, however, almost annihilates these peaks, as shown in Table III. However, as the excitation of Cu-K also decreases with the filter, the best compromise was obtained with the 2mm-filter, which lead to the largest Cu-K areas.

Table III – Effect of PMMA filter with Oxford Cr-tube for approximately the same photon flux on the detector (live time = 500s)

PMMA thickness	current mA	total counts	Cr-K area	Cu-K area
no filter	.010	3851400	1324680	3320
2 mm	.050	3914384	76896	6972
4 mm	.070	4094224	1476	5740

3.2 Pseudo-internal reference peaks

Dispersion of results was examined for the calibrating process. Relative standard deviations for the two preparation methods and using two different pseudo-internal reference peaks are compared in Table IV, for samples with 20 ppm added copper. For the detector of spectrometer A, strong Zr-K and L peaks and weak Hf-K peaks are generated in the spectra by the Zr collimator (Hf is a usual contamination of Zr). When no strong characteristic peaks from the sample are generated above Zr-K and Hf-K absorption edges, their excitation is basically due to the scattering of the incident beam by the sample. Therefore, their areas are sensitive to the flux of incident photons and to the sample-detector distance, and can be used as a pseudo-internal reference for similar samples. One observes in Table II that both peaks are equally effective in improving the relative standard deviation.

Table IV - Standard deviations observed for three similar samples with pseudo-internal references from Ketek detector for 25 ppm added copper ("full emulsion" preparation method)

	Cu	Cu/Zr	Cu/Hf
Average area or ratio	2124	6.16E-03	0.683
standard deviation %	18.1	13.0	12.9

3.3 Comparison of preparation methods for calibration-samples

The two preparation strategies of Cu/Co-added biodiesel reference samples lead to similar calibration curves, but the "methanol-evaporation" procedure lead to smaller values of dispersion than the "full-emulsion" procedure, as can be seen in Table V. Therefore, a smaller number of essays are necessary with the second method to reach the same confiability level.

Table V - Standard deviations observed with two different preparation methods, with spectrometer B

	average area	standard deviation %
"full-emulsion" method	2955	7.9
"methanol-evaporation" method	3110	5.1

3.4 Calibration constants and analysis of several samples of biodiesel from the corrosion test

Figure 4 shows the determination of calibration constants for added copper in B100 biodiesel, for spectrometer A, with the "full emulsion" preparation method. Each point is an average of five measurements, and a constant value corresponding to previous copper in the biodiesel was removed from the data. A good R^2 value was observed. Table VI presents the results obtained from samples of biodiesel from the corrosion tests of copper and brass in three different conditions: light at room temperature, darkness at room temperature, and darkness at 55°C. Results of zinc content after the exposure of brass are also shown. They were obtained in the same way as those of copper, with previous calibration using $ZnSO_4.4H_2O$. These results are compared in the table with the thickness losses of the metallic samples in those essays. One observes that the results are coherent, with a strong reduction of corrosion in darkness at 55°C when compared to room temperature behavior, even under light. One observes also that the biodiesel was much more aggressive to brass than to copper.

Table VI - Results from corrosion tests

	EDXRF of biodiesel			thickness loss (μm/year)	
	copper	brass		copper	brass
Light, RT	69 ppm Cu	115 ppm Cu	15 ppm Zn	5.8	22.0
Darkness, RT	67 ppm Cu	116 ppm Cu	12 ppm Zn	4.4	20.6
Darkness, 55°C	15 ppm Cu	8 ppm Cu	1 ppm Zn	.5	.6

4. Conclusions

It was observed that EDXRF is an adequate analytical technique for identifying and quantifying Cu and Zn ions in biodiesel, in contents above around 10 ppm. W-tubes, although providing stronger excitation of Cu-K peaks, may present problems if the W-L scattered peaks are strong and reach the detector, because they overlap with Cu-K peaks. In our specific spectrometers, this was not a problem with the Ital-Structures W-tube, which presented weak W-L peaks in the beam. A detector with lower detection angle, as our Ketek one, is also more adequate in this question. For the other detector, however, an external collimator may improve this behavior.

Regarding Cr-tubes, the Cr-scattered peaks do not overlap with Cu-K peaks. However, they are very strong and may impose that a low current is used in order not to saturate the detector. This was avoided with a PMMA filter.

With the Ketek detector, the Hf-L peaks probably originated from the Zr collimator overlapped with Cu-K peaks. A careful fitting process, however, allows Cu-K areas to be reasonably well determined, as concluded from the acceptable standard deviations observed and from the good correlations between the areas and the added Cu contents.

Then, although the more recent Amptek detector had lead to smaller standard deviations, the older Ketek detector can be successfully used for this purpose.

One observes, too, that the preparation of calibration samples should be made very carefully. As some polar liquid is necessary for a good distribution of added Cu in the biodiesel, it is necessary that an homogeneous emulsion is obtained, or that the polar liquid is eliminated from the biodiesel prior to the essays, leading the added Cu to be homogeneously dispersed in the oil. In our experiments, evaporation of methanol lead to better results than trying to get an stable emulsion by stirring.

Finally, the results from the biodesel samples with unknown Cu and Zn contents were sensitive to the essay variables and were coherent with the weight-loss results.

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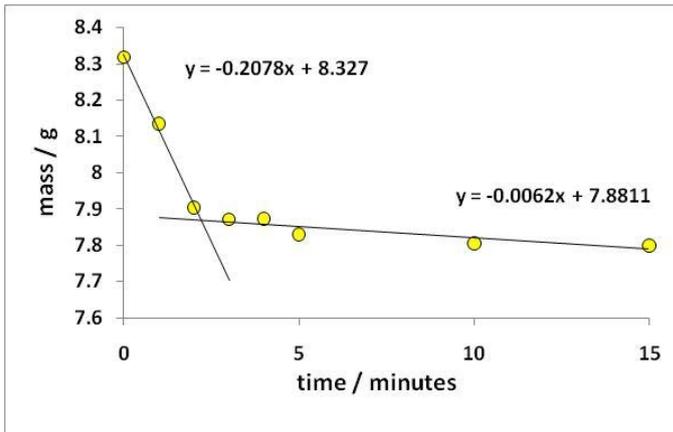
Figure 1 - Weight-loss measurements of methanol-biodiesel emulsion at 70°C
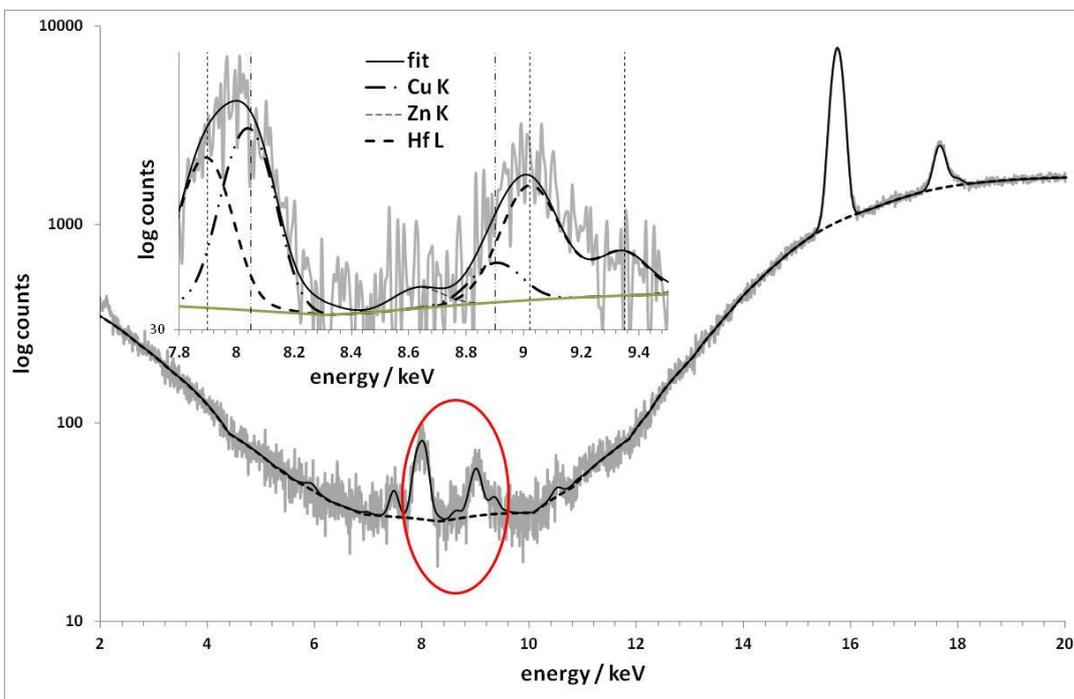
Figure 2 - Spectrum of 25ppm added-Cu biodiesel by spectrometer A. In the inset, details of the fitting of Hf-L, Cu-K and Zn-K peaks. The thin vertical lines indicate three Hf-L peaks and two Cu-K peaks.
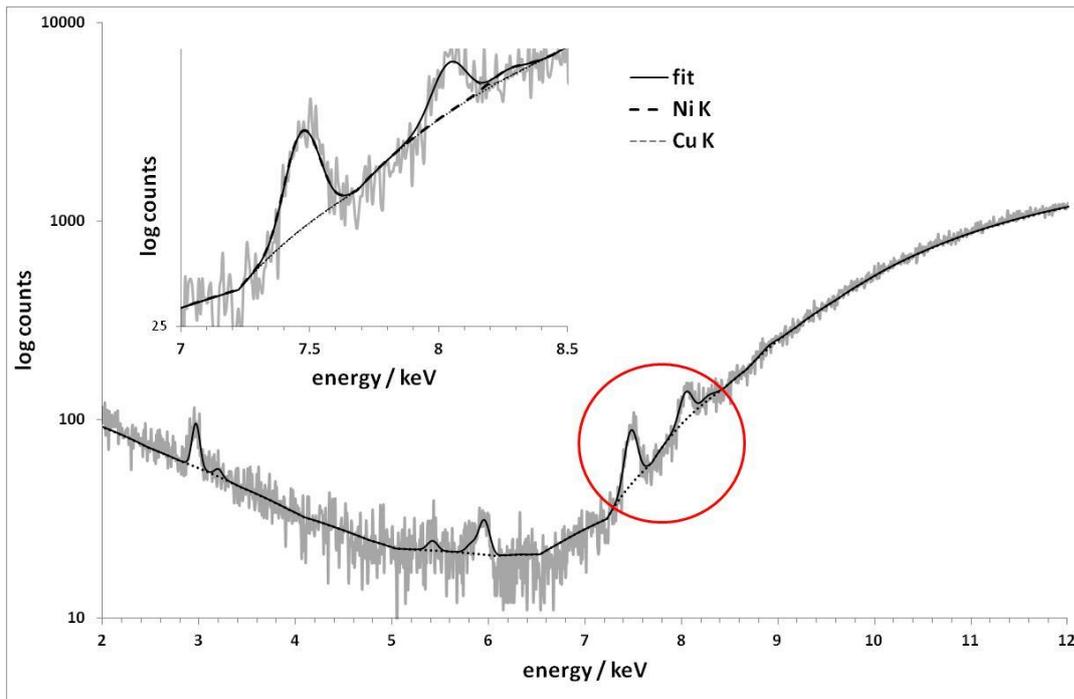
Figure 3 - Spectrum of 25ppm added-Cu biodiesel by spectrometer B with Cr-tube and 4mm-PMMA filter. In the inset, details of the fitting of Ni-K and Cu-K peaks.
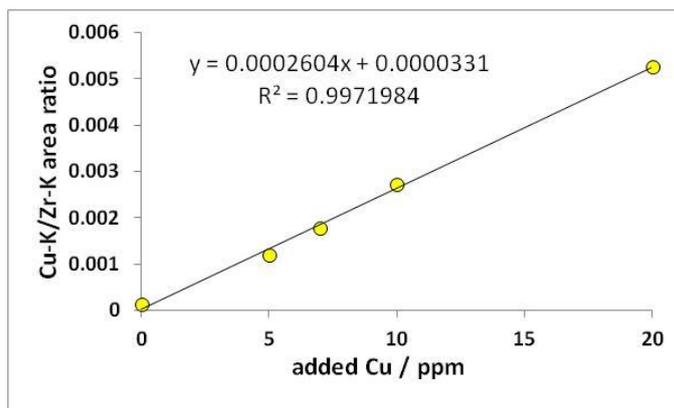

Figure 4 - Correlation between the Cu-K peak areas and the Cu addition. Cu-K areas were divided by the area of Zr-K, used as a pseudo-internal reference.