

1 **Analysis of waste electrical and electronic equipment (WEEE) using laser**  
2 **induced breakdown spectroscopy (LIBS) and multivariate analysis**

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4 Miguel Ángel Aguirre<sup>a</sup>, Montserrat Hidalgo<sup>a</sup>, Antonio Canals<sup>a</sup>, Joaquim A. Nóbrega<sup>b</sup> and E.  
5 R. Pereira-Filho<sup>\*b</sup>

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7 <sup>a</sup>Departamento de Química Analítica, Nutrición y Bromatología, Universidad de Alicante,  
8 Apdo. 99, Alicante E-03080, Spain.

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10 <sup>b</sup>Departamento de Química, Universidade Federal de São Carlos, PO Box 676, 13560-970 São  
11 Carlos, SP, Brazil. \* erpf@ufscar.br

12

13 \*Corresponding author

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1 **ABSTRACT:** This study shows the application of laser induced breakdown spectroscopy  
2 (LIBS) for waste electrical and electronic equipment (WEEE) investigation. Several emission  
3 spectra were obtained for 7 different mobiles from 4 different manufacturers. Using the  
4 emission spectra of the black components it was possible to see some differences among the  
5 manufacturers and some emission lines from organic elements and molecules (N, O, CN and  
6 C<sub>2</sub>) led to the highest contribution for this differentiation. Some polymeric internal parts in  
7 contact with the inner pieces of the mobiles and covered with a special paint presented a  
8 strong emission signal for Cr. The white pieces presented mainly Al, Ba and Ti in their  
9 composition. Finally, this study developed a procedure for LIBS emission spectra using  
10 chemometric strategies and suitable information can be obtained for identification of  
11 manufacturer and counterfeit products. In addition, the results obtained can improve the  
12 classification for establishing recycling strategies of e-waste.

13

## 1 1. INTRODUCTION

2 The increasing and continuous use of electronic and electrical devices is one of the factors for  
3 the generation of a great amount of residues in several countries. These materials are  
4 commonly named WEEE (Waste Electrical and Electronic Equipment) or simply e-waste. A  
5 general perspective can be observed for mobiles, where nowadays it is estimated that around  
6 100 millions of these equipments are discarded every year worldwide. This panorama is  
7 generating several problems: (i) with the technological development, new materials are  
8 introduced every year in the market and it is not a simple task to predict e-waste elemental  
9 composition and identification of hazardous elements<sup>1-4</sup>; (ii) e-waste is subject to illegal  
10 commerce since these materials are indiscriminately sent to developing countries in Africa or  
11 Latin America; (iii) in several countries there are not regulations for environmental recycling  
12 procedures to the recovery of precious and/or valuable metals and workers are in contact with  
13 toxic elements (Cd, Cr, Hg, Pb, among others) from the printed circuit board (PCB)<sup>2, 5-8</sup>.

14 Xinhui *et al.*<sup>9</sup> studied a low-tech recycling workshop in China and they found  
15 bisphenol A concentrations to be around 5 orders of magnitude higher when compared with  
16 indoor and outdoor environments in the world. In addition, the authors identified high Cd, Ni  
17 and Pb concentrations in the particulate matter (PM). The chemical identification of the  
18 composition of these materials is an important step to lead to the establishment of safe  
19 recycling procedures and final disposal of e-waste. In 2009 Nnorom and Osibanjo<sup>10</sup>  
20 determined Ag, Cd, Pb and Ni in plastic housing of mobile phones and these authors observed  
21 concentrations varying from 4.6 mg/kg (for Cd) to 12,500 mg/kg (for Ag). Yamane *et al.*<sup>11</sup>  
22 characterized and compared the PCB's from mobile phones and computers and they showed  
23 that there are differences of metals composition (63 % w/w in mobile phones and 45% w/w in  
24 computers). This topic is of concern in several countries and some articles about the situation  
25 in Germany<sup>12,13</sup>, Norway<sup>14</sup>, Austria<sup>7, 15</sup> and Brazil<sup>16</sup>, reporting the importance of recycling

1 instead incineration and the need of a new Brazilian law for solid waste management, were  
2 identified in the literature.

3 Several analytical techniques have been applied to the identification of hazardous  
4 compounds in electronic devices. Santos *et al.*<sup>17</sup> determined Cd, Cr, Hg and Pb in plastics  
5 from e-waste using inductively coupled plasma mass spectrometry (ICP MS) and the authors  
6 observed the highest concentrations for Cr (from 16 to 43 mg/kg). In another study from this  
7 same group<sup>18</sup> these authors used electrothermal atomic absorption spectrometry (ETAAS) for  
8 direct slurries analysis of plastics samples and it was reported Sb levels from 0.2 to 1.65%  
9 (w/w).

10 Additionally, using analytical techniques and chemometric tools, classification models  
11 can be proposed to identify the origin or the manufacturer of e-waste from the illegal  
12 commerce. Laser IBS can help in the accomplishment of these tasks because the analytical  
13 throughput is high and does not require extensive sample preparation<sup>19</sup>. In addition, the nature  
14 of the chemical data obtained requires the use of mathematical and statistical approaches for  
15 better interpretation, initial exploratory analysis and also for data mining<sup>20-25</sup>. The successful  
16 combination of LIBS and chemometric strategies was demonstrated by Shunchun *et al.*<sup>26</sup>  
17 where the authors presented a regression model using PLS (Partial Least Squares) for ash  
18 determination in coal. The versatility of LIBS was also demonstrated for sugar cane leaves<sup>27</sup>,  
19 soil<sup>28</sup>, toys<sup>29</sup> and warfare agent simulants<sup>30</sup> classification, unburned carbon determination in  
20 fly ash for furnace efficiency evaluation<sup>31</sup>, wastewater analyses<sup>32</sup>, Cr determination in dyed  
21 wool fabric<sup>33</sup> and remotely identify Martian rock<sup>34</sup>.

22 The aim of the present study is to show the potentialities of the combination of LIBS  
23 and chemometric strategies for e-waste characterization and classification. Some mobile  
24 samples from different manufacturers and countries were selected as a case study and  
25 important aspects are here highlighted.

## 2. EXPERIMENTAL SECTION

**2.1. Samples.** Seven mobiles from different manufacturers, models and colors were selected in order to show the applicability of LIBS for e-waste analysis and how to obtain useful information from the emission spectra. Table 1 shows the mobiles main characteristics. Four manufacturers were selected with 6 different models and the color of most analyzed parts were black. The mobiles were dismantled, external and internal polymers were cut (around 1 mm thickness) and analyzed as well as the PCBs.

**2.2. LIBS system, data set collection and chemometric evaluation.** The LIBS system was composed by a Nd:YAG laser (model HYL Handy-YAG, Q-switched, Quanta System S.P.A., Varese, Italy), emitting pulses of 180 mJ energy (pulse width 10 ns FWHM) at 1,064 nm. The laser was operated in single shot mode and the laser beam was focused on the samples by a biconvex lens with a 100 mm focal length. The emission of the laser-induced plasmas was collected using a fiber optic and detected by a five channels spectrometer (model AvaSpec-2048-SPU, Avantes, Apeldoorn, The Netherlands) covering wavelengths from 197.146 to 852.190 nm (8192 variables). A delay system consisting on two pulse generators (Digital delay/pulse generator, model DG 535, Stanford Research Systems, Inc. and 1 Hz-50 MHz pulse generator, model PM-5715, Philips) was used for synchronization of laser firing and data acquisition. Spectra were collected 1.3  $\mu$ s after the plasma generation, with 1 ms acquisition time (minimum time settings available on the spectrometer). A LG laptop (Intel Core 2 processor, 1.00 GB of RAM and Windows Vista) equipped with AvaSoft (Avantes, version 7.5.3 Full software) was used for data acquisition and visualization. Figure 1 shows a pictorial description of the used system.

Several spectra were acquired from a single laser shot at different points of the samples and two approaches for data treatment were applied. First, information from the surface was

1 obtained in order to identify general trends in the mobiles samples. In this case, the emission  
2 spectrum from the first pulse was collected. Later, after 10 successive pulses in the same  
3 sample position, spectrum from the bulk was obtained in order to identify the origin of the  
4 samples and to establish a fingerprint of the manufacturers. The bulk of the samples was  
5 identified after some initial experiments and it was concluded that this part was reached after  
6 emissions of elements mainly located on the surface disappear from the spectra and the  
7 emissions of elements located in the bulk become constant.

8 After data collection, a procedure to identify useful information was performed. Figure  
9 2 shows a description of the mathematical procedures performed. Two different strategies  
10 were applied. In the first one a Savitzky-Golay digital filter for first derivative calculation was  
11 performed, and later on the data was mean centered. In the second strategy,  $\log_{10}$  was  
12 calculated for each variable and then mean centered. This second approach was based in the  
13 procedure described by Pereira *et al.*<sup>35</sup> and was used for investigating manufacturers.  
14 Calculations were performed with Matlab 2009a (The Math Works, Natick, USA).

15

### 16 **3. RESULTS AND DISCUSSION**

17 **3.1. Polymers exploratory analysis.** For qualitative purposes, that is the goal of this study,  
18 typical RSD (Relative Standard Deviation) values ranged from 18 to 40%. These values were  
19 calculated taking the signals intensity at all wavelength range studied and the average number  
20 of replicates was 4. Otherwise, for quantitative purposes, the same calculation using 21 peak  
21 areas at relevant wavelengths was also performed and the RSD values ranged from 10 to 17%  
22 ( $n = 4$  in average). In both cases the RSD values were higher for surface measurements than  
23 for the bulk ones.

24 An initial exploratory analysis was performed using 38 spectra (from the surfaces and  
25 the bulk of the samples) and 8192 variables (197.146 - 852.190 nm). The first two PC's

1 accounted 77% of the explained variable and Figure 3 shows scores when the first derivate  
2 with 5 windows was applied (Strategy 1, see Figure 2). It can be seen that the silver and  
3 brown internal parts of mobiles 5 and 3, respectively, have a different composition when  
4 compared with the other polymeric pieces. On the other hand, it is possible to see also two  
5 different clusters, one related to all black and transparent parts of mobiles, no matter the  
6 mobile origin, and the other related to white parts (mobile 6).

7 After this initial exploratory analysis some particularities of the polymeric pieces are  
8 highlighted. Figure 4 for instance shows the Si (4a) and Ti (4b) emission lines for the black  
9 pieces (mobiles 1 - 5). These pieces presented similar results and Si (4a) was observed in both  
10 the surface (black line) and the bulk (red line) parts of the polymers. On the other hand, Ti  
11 (4b) was only detected in the surface of the polymers. The brown part of mobile 3 was  
12 characterized by the presence of Ag (Figure 5) only in the surface. The white polymers  
13 presented Ti (Figure 6a), Al (Figure 6b) and Ba (Figure 6c) in the surface and bulk parts.

14 The silver part from mobile 5 presented intense Cr signal (Figure 7) only in the inner  
15 part in contact with pieces of the mobile. Probably this part performs some special function in  
16 the mobile operation.

17

18 **3.2. Manufacturers identification.** Another possibility investigated was the manufacturer  
19 identification using LIBS emission spectra. In this case, only the black pieces were analyzed  
20 and a matrix with 168 spectra from the bulk and 8192 variables was organized. The best  
21 manufacturers discrimination was obtained after using  $\text{Log}_{10}$  data transformation and mean  
22 centering pre-treatment (see details in Figure 2). An initial PCA was calculated and the  
23 loading values were used for variables selection. After that 3532 variables were selected.

24 Figure 8 shows the scores (8a) and loadings (8b) plots when the black parts of 6  
25 mobiles (mobiles 1, 2, 3, 4, 5 and 7) were studied. Three tendencies can be observed in Figure

1 8a: (i) the black fragments from mobile 4 (red circles) were separated from the other pieces  
2 due to the high signals obtained for K I lines according to loadings values presented in Figure  
3 8b; (ii) mobiles 1, 2 and 3 were from the same manufacturer and their pieces were spread  
4 along PC1 with some samples presenting high values for this PC. These samples were mainly  
5 characterized by the presence of Na I, Ca II, C<sub>2</sub> I and CN I lines; (iii) mobiles 5 and 7 were  
6 clustered at negative values of PC1 and, in this case, these samples were mainly correlated to  
7 N I and O I lines.

8         According to the results presented it is possible to conclude that few lines are  
9 responsible for polymers characterization and also typical constituents of organic components  
10 (C, O, N and CN) are important for their distinction.

11

12 **3.3. PCB's characterization.** The same procedure described for the collection of spectra in  
13 the polymers was used for the PCB's. In this type of samples the bulk part is much richer in  
14 analytical signals than the surface (Figure 9). Copper, Ba, Si and Mg were observed in the  
15 bulk part. Probably these elements have insulation properties and the presence of Cu in PCBs  
16 seems obvious due to the electrical connections. In surface analysis, Ba, Si and Mg signals  
17 were also appreciable; however, Cu signal was almost negligible (see Figure 9).

18

19 **3.4. WEEE and LIBS outlook.** The use of LIBS for WEEE investigation opens some  
20 perspectives to generate a fast and reliable panorama of the WEEE composition. In addition,  
21 the LIBS system can be miniaturized and portable devices are nowadays available in the  
22 market. When compared with the procedures already described in the literature and  
23 recommended by the legislations, such as acid digestion<sup>11</sup> or use of the samples in the form of  
24 slurries<sup>18</sup> in combination with spectroanalytical techniques like ICP MS and ICP OES (ICP  
25 optical emission spectrometry), the combination of LIBS and WEEE analysis is also attractive



1 because the initial steps related to sample preparation are drastically shortened. On the other  
2 hand, the LIBS technique for quantitative analyses presents some challenges, such as the use  
3 of solid standards, matrices effects, and the laser interaction with different material. In  
4 addition, when compared with X-ray fluorescence (XRF) the LIBS system does not require a  
5 vacuum system for detecting light elements (C, N, and O) and by using a single pulse  
6 inorganic and organic fingerprints can be obtained. Finally, due to the emission spectra  
7 complexity and the huge quantity of data that can be obtained in just one pulse the use of  
8 chemometric tools is sometimes mandatory in order to deal with the data and extract useful  
9 information from them.

10 The combination of LIBS and chemometric strategies provided better data  
11 interpretation and visualization. In addition, the whole spectra profile was used and not only  
12 the inorganic elements but also the organic components can help in the manufacturer  
13 identification. This study opens possibilities for e-waste characterization providing  
14 information for supporting recycling procedures and also identification of counterfeit.

15

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## 23 **REFERENCES**

24 (1) Cui, J.; Forssberg, E. Mechanical recycling of waste electric and electronic  
25 equipments: a review. *J. Hazard. Mater.* **2003**, *B99*, 243-263.

- 1 (2) Cui, J; Zhang, L. Metallurgical recovery of metals from electronic waste: a review. *J.*  
2 *Hazard. Mater.* **2008**, *158*, 228-256.
- 3 (3) Ernst, T.; Popp, R.; Wolf, M.; van Eldik, R. Analysis of eco-relevant elements and  
4 noble metals in printed wiring boards using AAS, ICP-AES and EDXRF. *Anal. Bioanal.*  
5 *Chem.* **2003**, *375*, 805-814.
- 6 (4) Wager, P. A.; Schluep, M.; Muller, E.; Gloor, R. RoHS regulated substances in mixed  
7 plastics from waste electrical and electronic equipment. *Environ. Sci. Technol.* **2012**, *46*, 628-  
8 635.
- 9 (5) Cui, J.; Forssberg, E. Characterization of shredded television scrap and implications  
10 for materials recovery. *Waste Manage.* **2007**, *27*, 415-424.
- 11 (6) Tsydenova, O.; Bengtsson, M. Chemical hazards associated with treatment of waste  
12 electrical and electronic equipment. *Waste Manage.* **2011**, *31*, 45-58.
- 13 (7) Wager, P. A.; Hischer, R.; Eugster, M. Environmental impacts of the Swiss collection  
14 and recovery systems for waste electrical and electronic equipment (WEEE): a follow-up. *Sci.*  
15 *Total Environ.* **2011**, *409*, 1746-1756.
- 16 (8) Morf, L. S.; Tremp, J.; Gloor, R.; Huber, Y.; Stengele, M.; Zennegg, M. Brominated  
17 flame retardants in waste electrical and electronic equipment: substance flows in a recycling  
18 plant. *Environ. Sci. Technol.* **2005**, *39*, 8691-8699.
- 19 (9) Xinhui, B.; Simoneit, B. R. T.; ZhenZhen, W.; Xinming, W.; Guoying, S.; Jiamo, F.  
20 The major component of particles emitted during recycling of waste printed circuit boards in a  
21 typical e-waste workshop of South China. *Atmos. Environ.* **2010**, *44*, 4440-4445.
- 22 (10) Nnorom, I. C.; Osibanjo, O. Toxicity characterization of waste mobile phone plastics,  
23 *J. Hazard. Mater.* **2009**, *161*, 183-188.

- 1 (11) Yamane, L. H.; Moraes, V.; Espinosa, D. C. R.; Tenório, J. A. S. Recycling of WEEE:  
2 characterization of spent printed circuit boards from mobile phones and computers. *Waste*  
3 *Manage.* **2011**, *31*, 2553-2558.
- 4 (12) Dimitrakakis, E.; Janz, A.; Bilitewski, B.; Gidakos, E. Small WEEE: Determining  
5 recyclables and hazardous substances in plastics. *J. Hazard. Mater.* **2009**, *161*, 913-919.
- 6 (13) Dimitrakakis, E.; Janz, A.; Bilitewski, B.; Gidakos, E. Determination of heavy  
7 metals and halogens in plastics from electric and electronic waste. *Waste Manage.* **2009**, *29*,  
8 2700-2706.
- 9 (14) Hertwich, E. C.; Roux, C. Greenhouse gas emissions from the consumption of electric  
10 and electronic equipment by Norwegian households. *Environ. Sci. Technol.* **2011**, *45*, 8190-  
11 8196.
- 12 (15) Salhofer, S.; Tesar, M. Assessment of removal of components containing hazardous  
13 substances from small WEEE in Austria. *J. Hazard. Mater.* **2011**, *186*, 1481-1488.
- 14 (16) Araújo, M. G.; Magrini, A.; Mahler, C. F.; Bilitewski, B. A model for estimation of  
15 potential generation of waste electrical and electronic equipment in Brazil. *Waste Manage.*  
16 **2012**, *32*, 335-342.
- 17 (17) Santos, M. C.; Nóbrega, J. A.; Cadore, S. Determination of Cd, Cr, Hg and Pb in  
18 plastics from waste electrical and electronic equipment by inductively coupled plasma mass  
19 spectrometry with collision-reaction interface technology. *J. Hazard. Mater.* **2011**, *190*, 833-  
20 839.
- 21 (18) Santos, M. C.; Nóbrega, J. A.; Baccan, N.; Cadore, S. Determination of toxic elements  
22 in plastics from waste electrical and electronic equipment by slurry sampling electrothermal  
23 atomic absorption spectrometry. *Talanta* **2010**, *81*, 1781-1787.
- 24 (19) Pasquini, C.; Cortez, J.; Silva, L. M. C.; Gonzaga, F. B. Laser Induced Breakdown  
25 Spectroscopy. *J. Braz. Chem. Soc.* **2007**, *18*, 463-512.

- 1 (20) Dingari, N. C.; Barman, I.; Myakalwar, A. K.; Tewari, S. P.; Gundawar, M. K.  
2 Incorporation of support vector machines in the LIBS toolbox for sensitive and robust  
3 classification amidst unexpected sample and system variability. *Anal. Chem.* **2012**, *84*, 2686-  
4 2694.
- 5 (21) Yaroshchyk, P.; Death, D. L.; Spencer, S. J. Comparison of principal components  
6 regression, partial least squares regression, multi-block partial least squares regression, and  
7 serial partial least squares regression algorithms for the analysis of Fe in iron ore using LIBS.  
8 *J. Anal. At. Spectrom.* **2012**, *27*, 92-98.
- 9 (22) Zhe, W.; Jie, F.; Lizhi, L.; Weidou, N.; Zheng, L. A multivariate model based on  
10 dominant factor for laser-induced breakdown spectroscopy measurements. *J. Anal. At.*  
11 *Spectrom.* **2011**, *26*, 2289-2299.
- 12 (23) Amador-Hernández, J.; Garcia-Ayuso, L. E.; Fernández-Romero, J. M.; Luque de  
13 Castro, M. D. Partial least squares regression for problem solving in precious metal analysis  
14 by laser induced breakdown spectrometry. *J. Anal. At. Spectrom.* **2000**, *15*, 587-593.
- 15 (24) Sirven, J.-B.; Pailloux, A.; M'Baye, Y.; Coulon, N.; Alpettaz, T.; Gossé, S. Towards  
16 the determination of the geographical origin of yellow cake samples by laser-induced  
17 breakdown spectroscopy and chemometrics. *J. Anal. At. Spectrom.* **2009**, *24*, 451-459.
- 18 (25) Flower, W. L.; Peng, L. W.; Bonin, M. P.; French, N. B.; Johnsen, H. A.; Ottesen, D.  
19 K.; Renzi, R. F.; Westbrook, L. V. A laser-based technique to continuously monitor metal  
20 aerosol emission. *Fuel Process. Technol.* **1994**, *39*, 277-284.
- 21 (26) Shunchun, Y.; Jindong, L.; Meirong, D.; Kai, C.; Junyan, L.; Jun, L. Extracting coal  
22 ash content from laser-induced breakdown spectroscopy (LIBS) spectra by multivariate  
23 analysis. *Appl. Spectrosc.* **2011**, *65*, 1197-1201.
- 24 (27) Nunes, L. C.; Braga, J. W. B.; Trevizan, L. C.; Souza, P. F.; Carvalho, G. G. A.;  
25 Santos Jr., D.; Poppi, R. J.; Krug, F. J. Optimization and validation of a LIBS method for the

- 1 determination of macro and micronutrients in sugar cane leaves. *J. Anal. At. Spectrom.* **2010**,  
2 25, 1453-1460.
- 3 (28) Pontes, M. J. C.; Cortez, J.; Galvão, R. K. H.; Pasquini, C.; Araújo, M. C. U.; Coelho,  
4 R. M.; Chiba, M. K.; Abreu, M. F.; Madari, B. E. Classification of Brazilian soils by using  
5 LIBS and variable selection in the wavelet domain. *Anal. Chim. Acta* **2009**, *642*, 12-18.
- 6 (29) Godoy, Q.; Leme, F. O.; Trevisan, L. C.; Pereira-Filho, E. R.; Rufini, I. A.; Santos Jr.,  
7 D.; Krug, F. J. Laser-induced breakdown spectroscopy and chemometrics for classification of  
8 toys relying on toxic elements. *Spectrochim. Acta Part B* **2011**, *66*, 138-143.
- 9 (30) Munson, C. A.; De Lucia Jr., F. C.; Piehler, T.; McNesby, K. L.; Miziolek, A. W.  
10 Investigation of statistics strategies for improving the discriminating power of laser-induced  
11 breakdown spectroscopy for chemical and biological warfare agent stimulants. *Spectrochim.*  
12 *Acta Part B* **2005**, *60*, 1217-1224.
- 13 (31) Shunchun, Y.; Jidong, L.; Jianping, Z.; Meirong, D. Analysing unburned carbon in fly  
14 ash using laser-induced breakdown spectroscopy with multivariate calibration method. *J.*  
15 *Anal. At. Spectrom.* **2012**, *27*, 473-478.
- 16 (32) Gondal, M. A.; Hussain, T. Determination of poisonous metals in wastewater collected  
17 from paint manufacturing plant using laser-induced breakdown spectroscopy. *Talanta* **2007**,  
18 *71*, 73-80.
- 19 (33) Pouzar, M.; Prusová, M.; Prokopčaková, P.; Cernohorsky, T.; Wiener, J.; Krejčová, A.  
20 LIBS analysis of chromium in samples of dyed wool fabric. *J. Anal. At. Spectrom.* **2009**, *24*,  
21 685-688.
- 22 (34) Sirven, J.-B.; Sallé, B.; Mauchien, P.; Lacour, J.-C.; Maurice, S.; Manhes, G.  
23 Feasibility study of rock identification at the surface of Mars by remote laser-induced  
24 breakdown spectroscopy and three chemometric methods. *J. Anal. At. Spectrom.* **2007**, *22*,  
25 1471-1480.

- 1 (35) Pereira, F. M. V.; Milori, D. M. B. P.; Venâncio, A. L.; Russo, M. S. T.; Martins, P.
- 2 K.; Freitas-Astúa, J. Evaluation of the effects of *Candidatus Liberibacter asiaticus* on inoculated
- 3 citrus plants using laser-induced breakdown spectroscopy (LIBS) and chemometrics tools.
- 4 *Talanta* **2010**, 83, 351-356.

**Table 1. Mobile samples description**











Sample identification	Coded manufacturer	Coded model	Origin	Polymers Color	Parts example	Remarks
Mobile 1	A	1	Brazil	Black only		These two mobiles are from the same manufacturer and model
Mobile 2	A	1	Brazil	Black only		
Mobile 3	A	2	Brazil	Black and brown (internal)	 	-
Mobile 4	B	3	China	Black only		-
Mobile 5	C	4	South Korea	Black with internal plating	 	-
Mobile 6	D	5	Hungary	White only	 	This mobile has a digital camera and a transparent polymer in the screen.
Mobile 7	D	6	Hungary	Black and gray (internal)		-

Figure caption

**Figure 1.** Pictorial description of the LIBS equipment.

**Figure 2.** Description of the data set mathematical treatment proposed. Two strategies were tested: use of first derivative and  $\log_{10}$ . The dotted squares depicted in the strategy 2 show the ranges of wavelengths used on the final discrimination study after PCA calculation.

**Figure 3.** Scores for PC1 *versus* PC2 for all pieces tested (black, white, transparent, brown and silver parts) from the mobiles studied.

**Figure 4.** Emission signals for Si (a) and Ti (b) obtained from black part. The black and red lines correspond to surface and bulk, respectively.

**Figure 5.** Emission signals for Ag obtained from the brown part of mobile 3. The black and red lines correspond to surface and bulk, respectively.

**Figure 6.** Emission signals for Ti (a), Al (b) and Ba (c) obtained from the white part. The black and red lines correspond to surface and bulk, respectively.

**Figure 7.** Emission signals for Cr obtained from the silver part of mobile 5. The black and red lines correspond to surface and bulk, respectively.

**Figure 8.** 3D view of the scores (a) and loadings (b) plots for the black polymers studied from 6 mobiles.

**Figure 9.** Emission spectra obtained from the PCB's from bulk (a) and surface (b).



Figure 1

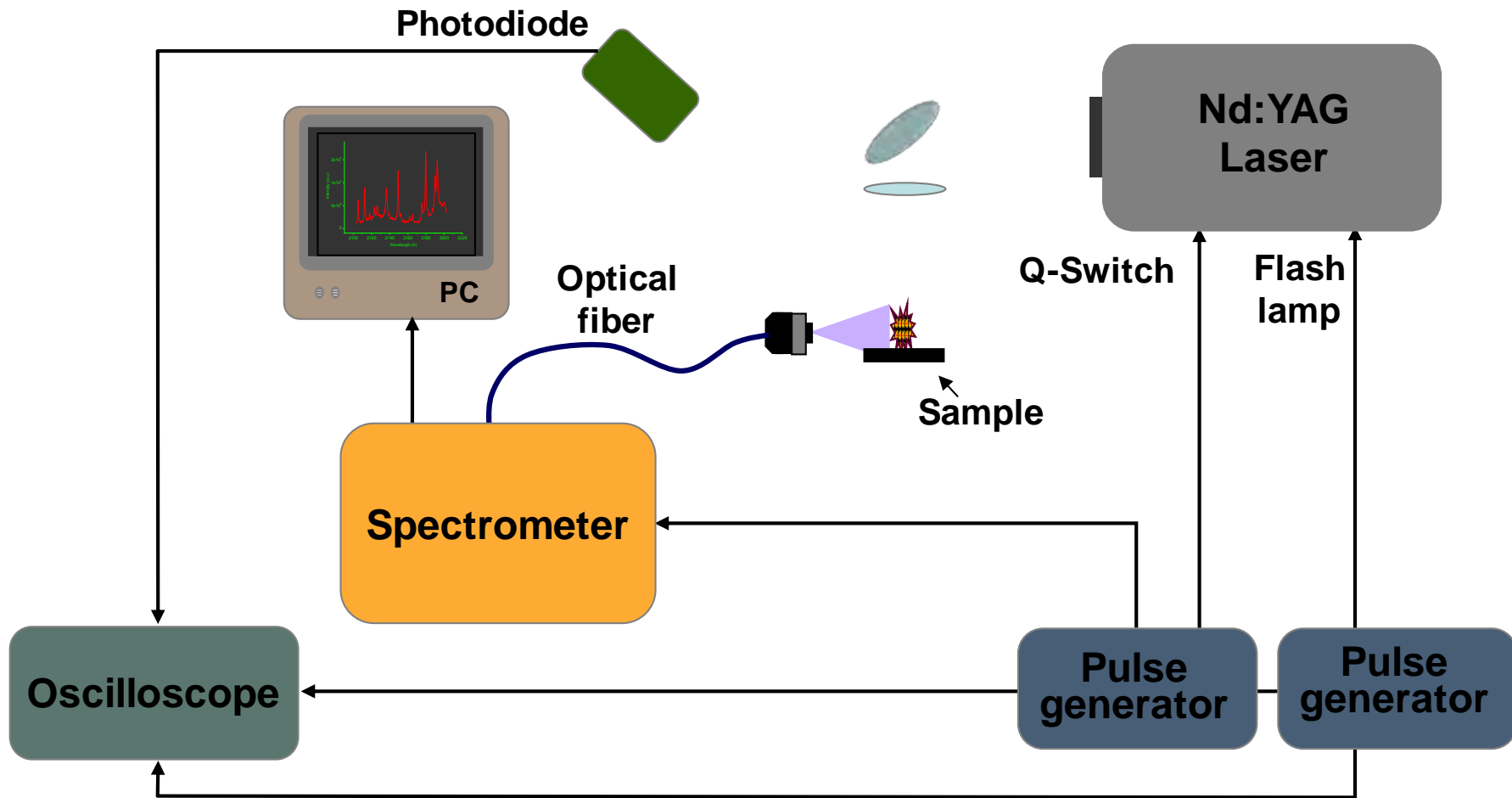


Figure 2

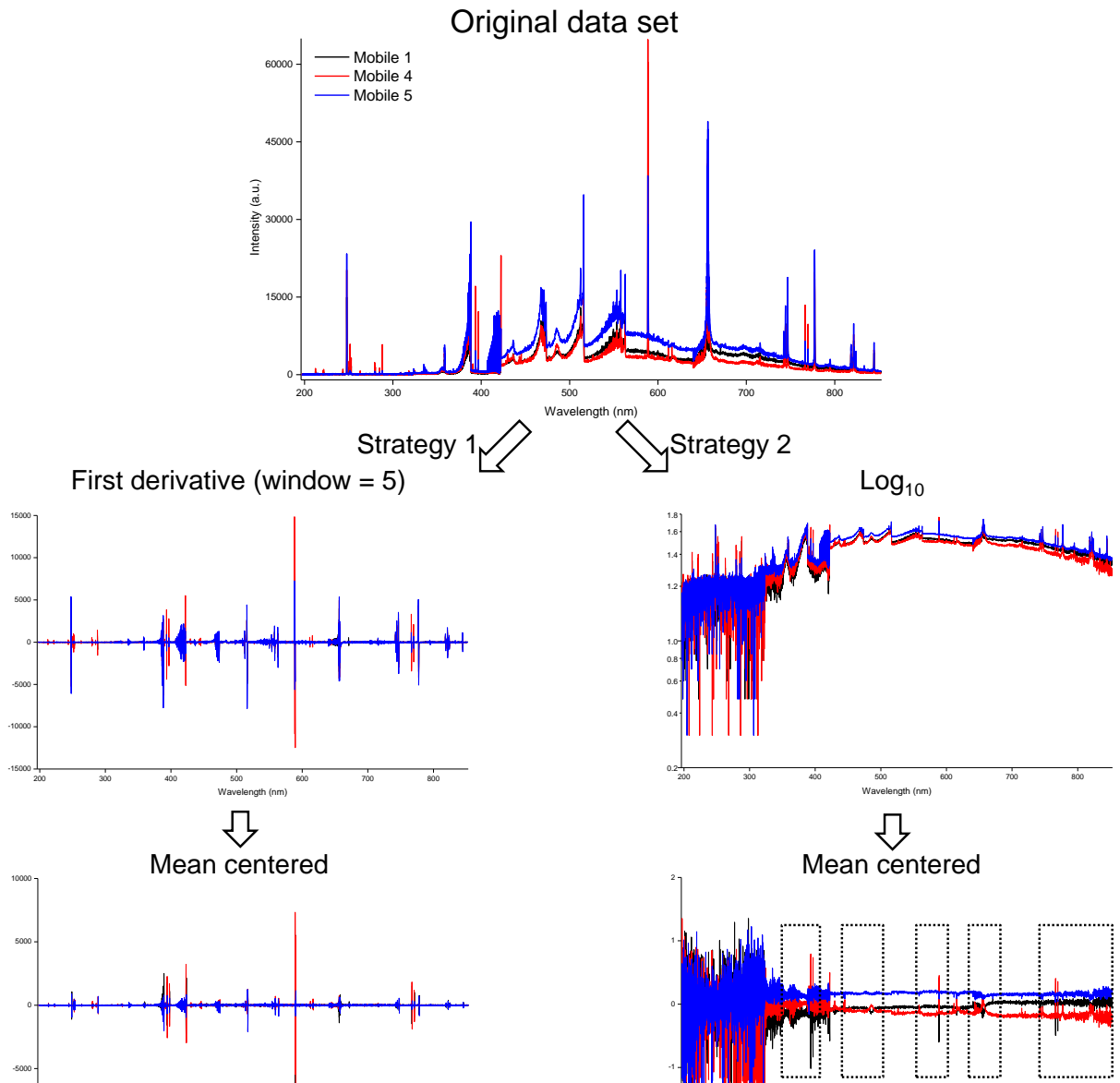


Figure 3

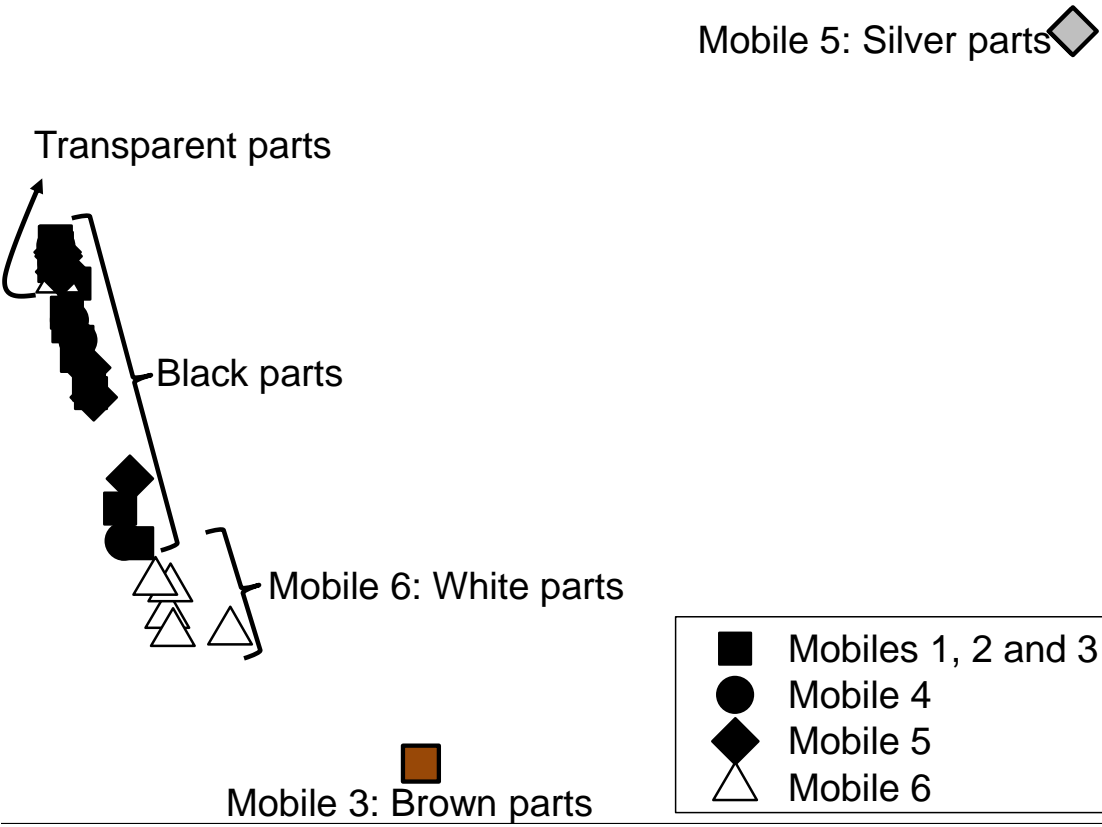


Figure 4

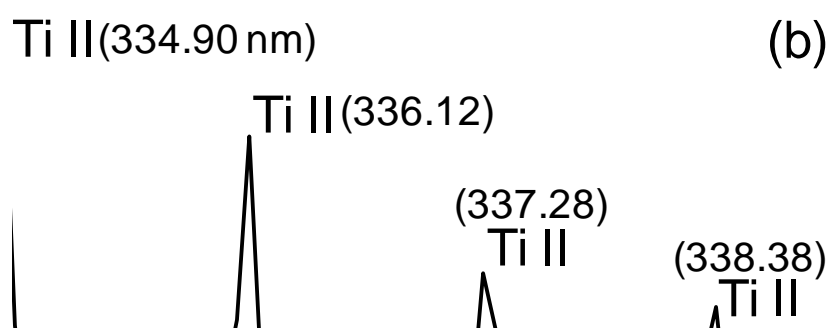
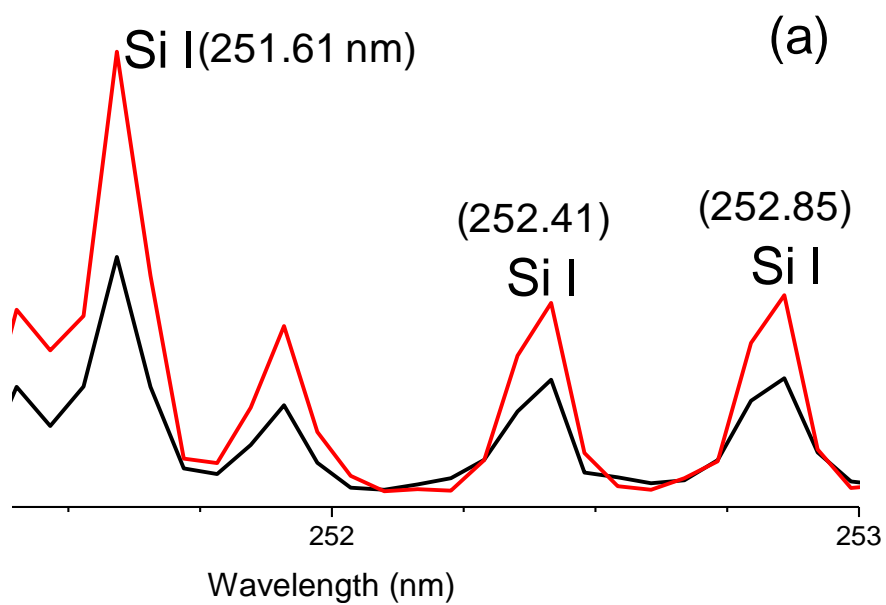



Figure 5

Ag II (201.60 nm)



Ag II  
(203.40)




Figure 6

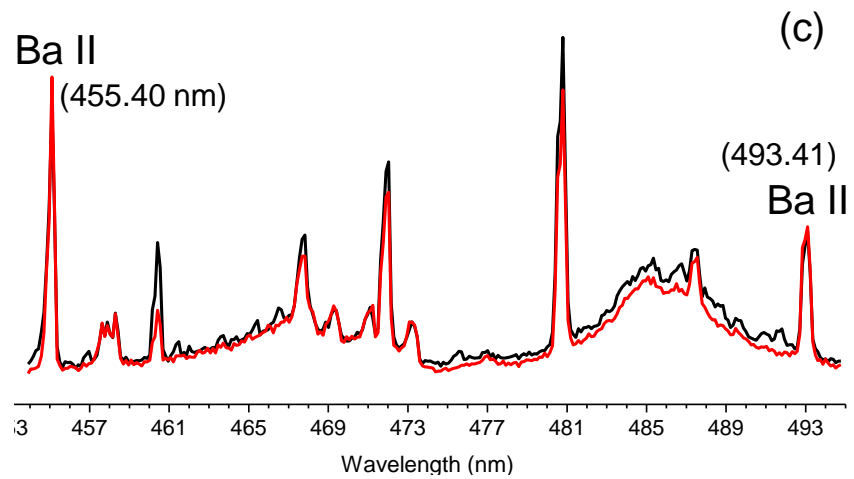
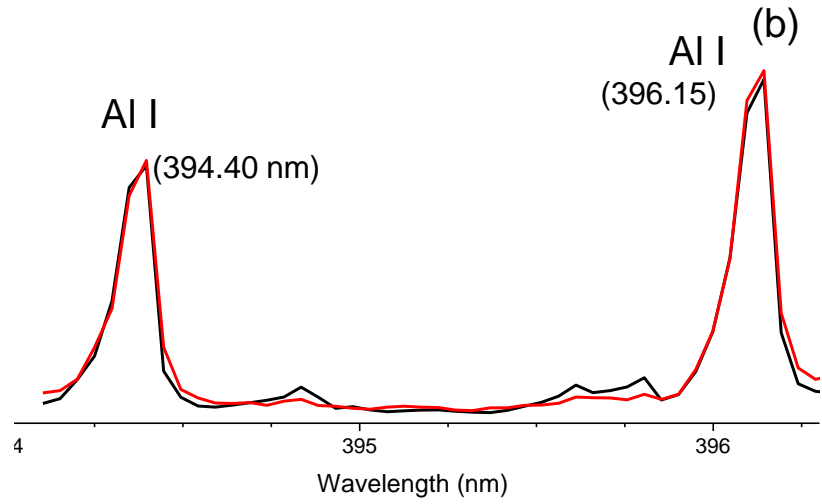
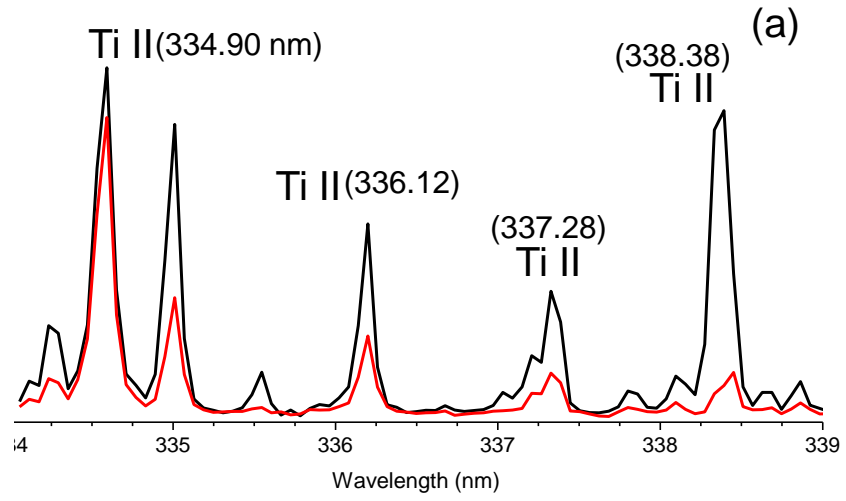


Figure 7

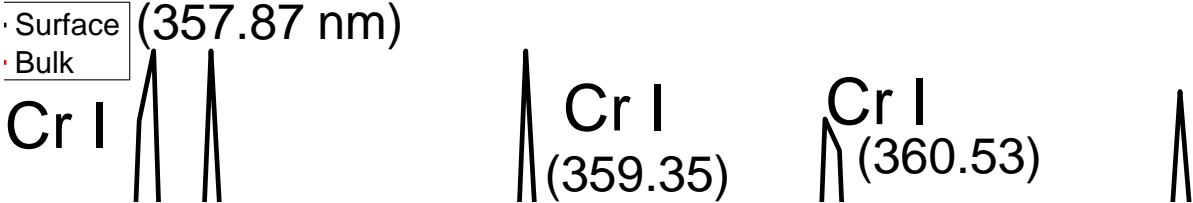


Figure 8a

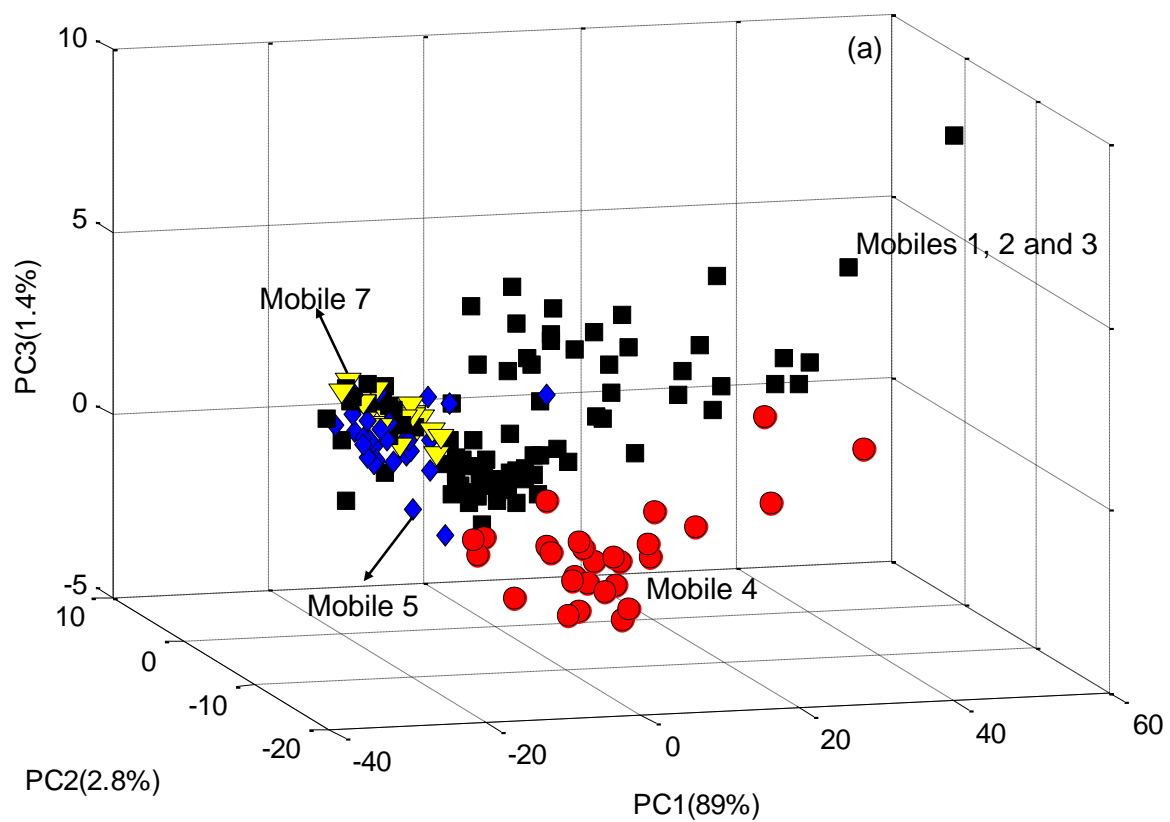




Figure 8b

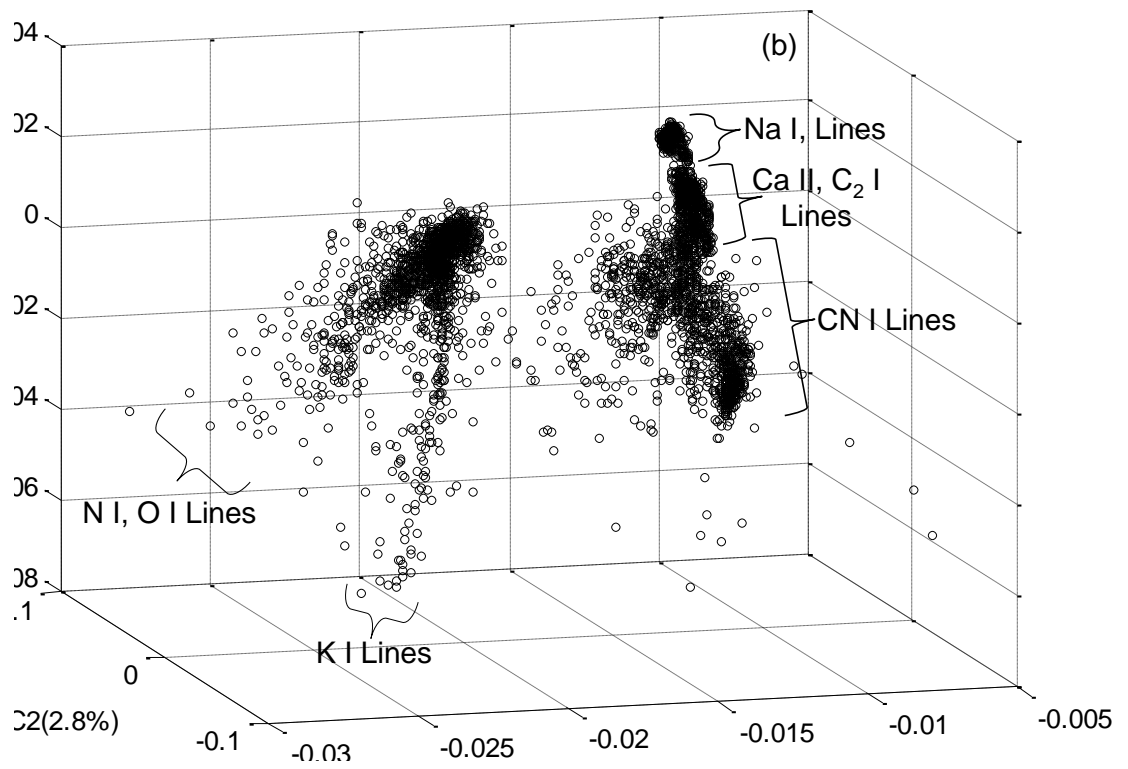


Figure 9

