

1 **Direct determination of Al and Pb in waste printed circuit boards (PCB) by**
2 **Laser-induced breakdown spectroscopy (LIBS): evaluation of calibration**
3 **strategies and economic - environmental questions**

4
5
6
7
8 Diego Victor Babos,^{1,2} Andrés Cruz-Conesa,¹ Edenir Rodrigues Pereira-Filho²
9 and Jesús Manuel Anzano^{1*}

10
11
12
13
14 ¹Laser Laboratory, Chemistry & Environment Group, Department of Analytical
15 Chemistry, Faculty of Sciences, University of Zaragoza, Pedro Cerbuna 12,
16 50009 Zaragoza, Spain

17 ²Group of Applied Instrumental Analysis, Department of Chemistry, Federal
18 University of São Carlos, São Carlos, São Paulo State, 13565-905, Brazil

19
20
21
22
23 *Corresponding author:

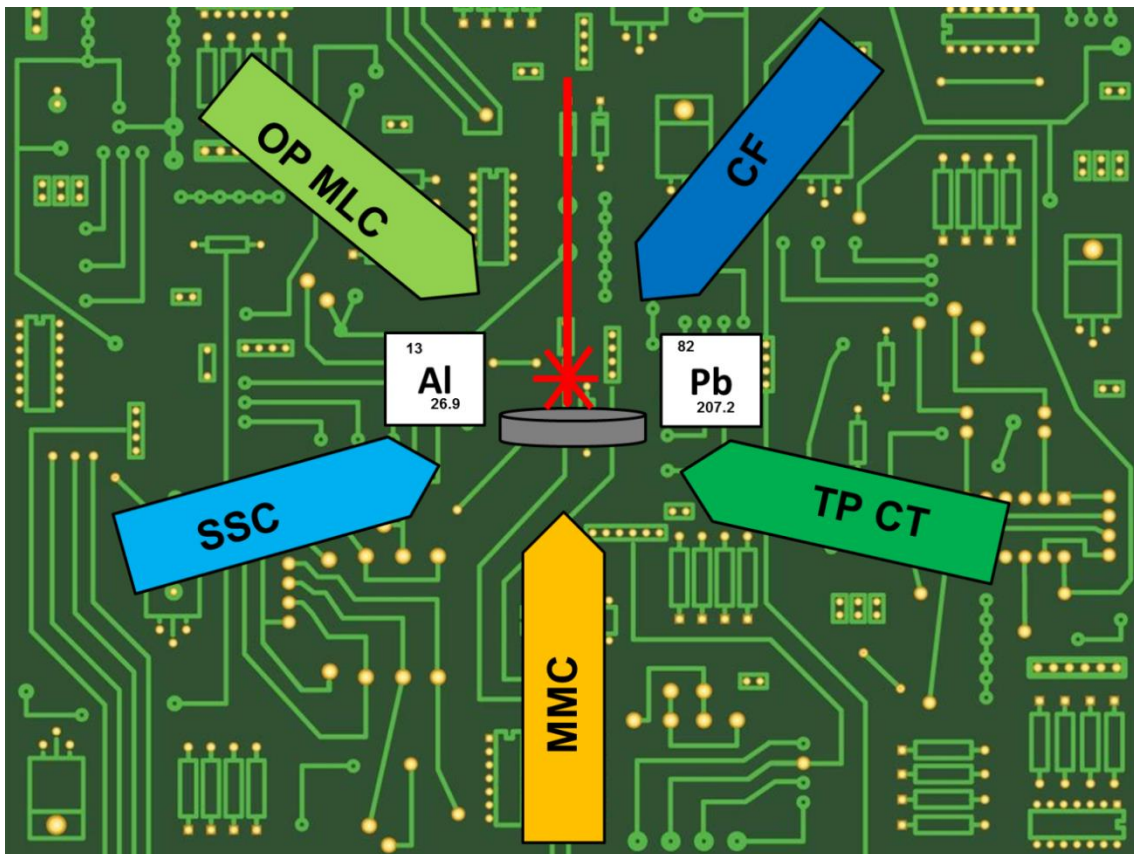
24 Jesús Manuel Anzano

25 Laser Laboratory, Chemistry & Environment Group, Department of Analytical
26 Chemistry, Faculty of Sciences, University of Zaragoza, Pedro Cerbuna 12,
27 50009 Zaragoza, Spain

28 Phone number: +34 9 7676 2684

29 E-mail: janzano@unizar.es (J. Anzano).

30 **Graphical abstract**



31
32 Evaluation of five calibration strategies for direct determination of recyclable and
33 toxic metals in waste PCB by LIBS
34

35 **Highlights**

- 36
- 37 • Fast and direct determination of Al and Pb in waste PCB by LIBS
 - 38 • Evaluation of five calibration strategies to overcome matrix effects by LIBS
 - 39 • Recent calibration strategies by LIBS were applied to determine Al and Pb in WEEE.
 - 40 • Pb concentration are 5 to 12 times higher than established by [Directive 2011/65/EU](#)
- 41
42
43
44
45
46
47
48

49 **Abstract**

50 Matrix-matching calibration (MMC), two-point calibration transfer (TP CT), one-
51 point and multi-line calibration (OP MLC), single-sample calibration (SSC) and
52 calibration free (CF) were evaluated in order to overcome matrix effects in laser-
53 induced breakdown spectroscopy (LIBS). These calibration strategies were
54 evaluated for direct determination of Al and Pb in waste printed circuit boards
55 (PCB) using direct solids analysis by LIBS. Each strategy has limitations and
56 advantages of its implementation, for the correction of matrix effects, so that it
57 allows elementary determination with adequate accuracy. The MMC and CF
58 proved to be excellent calibration strategies for the determination of strategic
59 (Al) and toxic (Pb) elements by LIBS, with good recoveries (ranging from 80 to
60 120%) and low relative standard deviation (RSD%) values. A detailed
61 discussion of the advantages and limitations of each of these five calibration
62 strategies evaluated for LIBS is presented in this study. Lead concentrations in
63 waste PCB samples are 5 to 12 times higher than established by Directive
64 2011/65/EU, and the samples analyzed contain between 3 and 55 g kg⁻¹ Al,
65 being an interesting economic and recycling source for this metal.

66

67

68 **Keywords:** WEEE; Toxic element; Environment pollution; Matrix-matching
69 calibration; Two-point calibration transfer; Calibration free; Single-sample
70 calibration; One-point multi-line calibration

71

72

73

74

75 **1. Introduction**

76 Contemporary society utilizes several types of high-tech electrical and
77 electronic devices and instruments. The study of waste electrical and electronic
78 equipment (WEEE) generation is therefore of great interest due to the
79 environmental, economic, recycling and reuse questions posed by this type of
80 waste (Costa et al. 2018a, Tansel, 2017). According to a study published in
81 2017, the projection of WEEE production is expressive (Andrade et al. 2019a,
82 2019b, 2019c, 2019d), being 52.2 million tons in 2021 (Baldé et al. 2017).

83 WEEE contains a diverse, complex and valuable composition,
84 consisting mainly of polymers, metals (base, toxic, noble and technological
85 elements) and ceramics. Printed circuit boards (PCB), which are part of the
86 electronic devices present in the WEEE, contain large amounts of valuable and
87 dangerous metals such as, for example, Al and Pb. Depending on the electronic
88 device, the metal content on PCBs can range from 2 to 19% Al and 1 to 3% Pb,
89 among others (Andrade et al. 2019b, Arshadi et al. 2018, Carvalho et al. 2015,
90 Perkins et al. 2014, Yamane et al. 2011, Yang et al. 2019). Aluminum and Pb
91 can be recycled, adding value to the WEEE and generating a source of income.
92 Lead is a toxic metal which in high concentrations can pollute the environment.
93 According to Directive 2011/65/EU, the maximum concentration allowed is 0.1%
94 by weight in homogeneous materials (RoHS, 2011).

95 The preparation of waste PCB samples for elemental analysis is a
96 challenging task due to the complexity of its composition and its refractory
97 character, being rich in oxides of Mg, Si and Ti, flame retardants, metals and
98 polymers. Thus, the need to use vigorous conditions in the acid decomposition
99 step is evident in order to obtain a homogeneous and representative solution for

100 subsequent quantitative analysis by conventional analytical techniques (Arshadi
101 et al. 2018).

102 LIBS technique has some advantages that could be used for the direct
103 analysis of waste PCBs, such as: minimum sample preparation, fast multi-
104 element analysis (μs), semi-destructive analysis (μg), and minimum waste
105 generation. A limitation of this technique is related to matrix effects, which may
106 compromise accuracy in quantitative analysis (Andrade et al. 2020, Carvalho et
107 al. 2018a, Costa et al. 2019, Cremers and Radziemski 2006, Gondal et al.
108 2010, Kim et al. 2013, Lasheras et al. 2011, Miziolek et al. 2006).

109 As the sample is analyzed integrally (analyte and matrix
110 simultaneously) by the LIBS instrument, the physicochemical properties of the
111 sample and the laser-sample and/or laser-plasma interaction may influence the
112 atomic/ionic/molecular emission phenomenon of the analyte (Cremers and
113 Radziemski 2006a, Miziolek et al. 2006). As in the majority of applications the
114 goal is quantitative analysis, requiring calibration standards in some strategies.
115 In addition, different matrix effects can occur in the plasma formed in the
116 samples and in the calibration standards. Consequently, the figures of merit of
117 the method can be jeopardized, and thus may make it impossible to determine
118 the analyte with satisfactory accuracy using direct solid analysis by LIBS (Hahn
119 and Omenetto 2010, Hahn and Omenetto 2012, Sattar et al. 2019).

120 Matrix effects (spectral and non-spectral) can be avoided or minimized
121 by careful peak selection or peak fitting of the analytical line and / or selecting
122 lines that do not exhibit spectral interference, in addition the use of high
123 resolution spectrometers in LIBS (makes it possible to identify and overcome
124 some spectral interferences) (Takahashi and Thornton 2017, NIST).

125 The non-spectral matrix effects are directly correlated to the physical
126 and chemical properties of the sample, and these effects are more difficult to
127 overcome because there are many possibilities of how the matrix may be
128 influenced by the analyte emission phenomenon (Cremers and Radziemski
129 2006a, Takahashi and Thornton 2017). The main non-spectral matrix effects
130 are related to the sample's irregular surface, inhomogeneous particle size and
131 humidity (Carvalho et al. 2018, Takahashi and Thornton 2017), the predominant
132 chemical composition of the sample (organic or inorganic forms) (Eppler et al.
133 1996), the temperature of the sample (Lednev et al. 2019), the pressure used to
134 compress the sample to form pellets (when necessary) (Popov et al. 2018), the
135 presence of easily ionizable elements (EIEs) (Morais et al. 2018, Popov et al.
136 2018), the interaction of the laser with the sample, heat of vaporization, thermal
137 conductivity, and the absorption coefficient, which affects the transport of an
138 ablated mass which will be vaporized and atomized into the plasma (Takahashi
139 and Thornton 2017), among others (Lasheras et al. 2013, Rezaei et al. 2018).
140 These matrix effects may contribute to the non-stoichiometric ablation of the
141 sample and thus reduce the possibility of using LIBS for quantitative analysis.

142 In order to overcome these matrix effects, univariate and multivariate
143 calibration strategies are used for LIBS: matrix-matching calibration (MMC)
144 (Costa et al. 2018b, Gomes et al. 2013, Vieira et al. 2018), standard addition
145 (SA) (Yi et al. 2016, Wu et al. 2019), one-point gravimetric standard addition
146 (OP GSA) (Babos et al. 2019), internal standardization (IS) (Aquino et al. 2016,
147 Carvalho et al. 2018b, Lasheras et al. 2013, Sperança et al. 2019) calibration
148 free (CF) (Calvacante et al. 2013, Ciucci et al. 1999, Li et al. 2019, Tognoni et
149 al. 2010), one-point and multi-line calibration (OP MLC) (Hao et al. 2018), multi-

150 energy calibration (MEC) (Andrade et al. 2019b, Augusto et al. 2019, Babos et
151 al. 2018, Carvalho et al. 2019, Castro et al. 2020, Fortunato et al. 2019), two-
152 point calibration transfer (TP CT) (Castro et al. 2020), and single-sample
153 calibration (SSC) (Yan et al. 2019).

154 It should be noted that many calibration possibilities are available for
155 LIBS, but the question is what is the best calibration strategy that could be
156 applied for the determination of Al and Pb in samples as complex, of
157 environmental and economic interest as waste PCBs. In order to answer this
158 question, five calibration strategies were selected and evaluated their
159 performance based on various parameters such as standard error (SE),
160 recovery and other figures of merit, considering the limitations and intrinsic
161 advantages of each calibration for overcoming matrix effects and for the
162 determination of these metals. Two strategies widely reported in the literature
163 (MMC and CF) and three that have recently been proposed (TP CT, OP MLC
164 and SSC) for calibration were evaluated for direct waste PCB analysis and
165 determinations of toxic (Pb) and strategic (Al) elements by LIBS.

166 **2. Experimental**

167 2.1. Instrumentation

168 LIBS spectra were obtained using an experimental set-up based on a
169 Q-switched Nd:YAG laser (BrilliantQuantel, model Ultra CFR) with a 1064 nm
170 wavelength, a 7.7 ns pulse duration and a maximum laser pulse energy of 50
171 mJ. The sample was placed inside a sample chamber and the laser beam
172 directly focused on it through a 150 mm focal length lens. The target surface
173 was positioned approximately 77 mm below the focal lens. The light emitted by
174 the plasma was collected by optic fibers connected to an Echelle spectrometer

175 (Andor Mechelle ME5000, 195 mm focal length, F/7, I/AI 5000). The
176 spectrometer is equipped with an intensified charge coupled device detector
177 (Andor iStar DH734, 1024 × 1024 pixels 13.6 × 13.6 μm² by pixel, 18 mm of
178 intensifier diameter). The wavelength and spectral resolution of the
179 spectrometer were calibrated using a low pressure mercury-argon lamp by
180 measuring both the spectral positions of the lines and their spectral profiles. The
181 LIBS system requires some instrumental parameters to be optimized such as
182 laser pulse energy, delay time, signal acquisition time and lens-sample
183 distance.

184 An inductively coupled plasma optical emission spectrometer (ICP
185 OES) (iCAP 7000, Thermo Scientific, Waltham, MA, USA) was used in the
186 determination of Al and Pb in printed circuit board waste after acid digestion of
187 the samples (n=3). The concentrations obtained were used as reference values
188 for the LIBS method. The emission lines monitored during ICP OES
189 determinations were Al 167.079 nm and Pb 216.99 nm using axial viewing
190 mode.

191 A scanning electron microscope (SEM) (JEOL JSM 6360-LV) (General
192 Research Support Service of the University of Zaragoza) with voltage up to 30
193 kV and a maximum resolution of 3.0 nm was used for the morphological surface
194 visualization of the waste PCBs. In order to perform the analysis, one waste
195 PCB sample was pelletized and selected (S2). Additionally, the pellet was
196 analyzed by SEM in order to obtain information about the crater formed by the
197 laser pulse and then to calculate both the irradiance and laser pulse fluence
198 values.

199 2.2. Reagents and samples

200 Standard solutions containing Al and Pb were prepared by diluting
201 standard stock solutions containing 1000 mg L⁻¹ (Specsol, São Paulo, Brazil),
202 and acidified with HNO₃ 10% v v⁻¹, and used for ICP OES analysis.

203 Six PCBs from desktop computers were collected at São Carlos (São
204 Paulo State, Brazil) and then ground in a knife mill (IKA, A11) (the particle size
205 was estimated to be lower than 500 µm) to obtain homogeneous and
206 representative samples. Approximately 200 mg of PCB samples were weighed
207 and compressed using a manual hydraulic press (Perkin Elmer IR Accessory
208 Hydraulic Press) with 10x10⁴ N for 2 min, to obtain pellets (n=3) for LIBS
209 analysis. It is necessary to press the sample to obtain cohesive pellets that
210 contribute to the reproducibility of the laser-sample interaction and consequently
211 to the precision of the measurements.

212 2.3. Sample preparation for determination of Al and Pb by ICP OES

213 The samples of PCBs were digested using microwave-assisted heating
214 for analysis and to obtain reference values of Al and Pb that were subsequently
215 used in the proposition of the calibration models and verification of the accuracy
216 of the proposed LIBS method. Masses of approximately 100 mg of PCB were
217 accurately weighed directly in the perfluoroalkoxy alkanes (PFA) digestion
218 vessels and microwave-assisted digested using a single reaction chamber oven
219 (UltraWave™, Milestone, Sorisole, Italy). Volumes of 5 mL of concentrated
220 HNO₃ were used as an oxidizing agent in the decomposition. The microwave
221 heating program was applied as follows: (1) 5 min to reach 100 °C, (2) 15 min
222 to reach 180 °C, (3) 15 min to reach 240 °C and (4) 7 min held at 240 °C.
223 Subsequently, the digests were diluted to 50.0 mL with distilled-deionized water

224 and filtered on qualitative filter paper 80 g m^{-2} (Unifil, Germany) for subsequent
225 ICP OES analysis.

226 2.4. Optimization of LIBS instrumental parameters

227 Using a full factorial design 2^3 with center and axial points, the
228 instrumental conditions (delay time, gate width and laser pulse energy) were
229 optimized. The variables studied were evaluated at five levels: delay time (0.01,
230 0.4, 1.2, 2.0 and $2.54 \mu\text{s}$), gate width (0.32, 1.0, 2.0, 3.0 and $3.68 \mu\text{s}$) and laser
231 pulse energy (20, 25, 35, 42.5 and 47.5 mJ). The variable levels were coded
232 between -1.68 (lower level) and +1.68 (higher level), with the central point
233 (coded as 0) used to calculate experimental errors. Table S1 presented at
234 supplementary material shows more details about the experimental design
235 performed. Due to experimental setup limitations the delay time values were
236 coded from -1.49 ($0.01 \mu\text{s}$) to 1.68 ($2.54 \mu\text{s}$) The S2 waste PCB sample
237 containing $55 \pm 3 \text{ g kg}^{-1}$ Al and $11.6 \pm 0.8 \text{ g kg}^{-1}$ Pb was used to optimize the
238 instrumental conditions used in the LIBS analyses. The Al and Pb reference
239 concentrations were obtained after microwave digestion and ICP OES
240 determinations.

241 The signal-to-background ratio (SBR) calculated for each monitored
242 emission line of Al and Pb (besides the lines of Ca, Fe, Si and Ti used for
243 calibration free) were used as responses of the factorial design. A mathematical
244 approach developed by Derringer and Suich (1980), based on desirability
245 functions applied to optimize multi-response experiments, was used in this
246 study. This strategy first converts each experimental response into an individual
247 desirability value (d_i), which ranges between $0 \leq d_i \leq 1$. In this case, $d_i = 1$
248 corresponds to a desired response (high SBR), while $d_i = 0$ represents a

249 response that is outside the acceptable region (the lowest SBR). The individual
250 desirability value was combined into a single response after an arithmetic mean
251 calculation (the overall desirability, OD). In this study, was exceptionally used
252 the arithmetic mean because some experiments resulted in $d_i = 0$.

253 2.5. Calibration strategies

254 Five calibration strategies were evaluated for the determination of Al
255 and Pb in waste PCB samples by LIBS. For all the calibration strategies, the
256 calibration standards and samples were pelletized ($n=3$) using approximately
257 200 mg of waste PCB. The resulting pellets were analyzed using 50 pulses in
258 different spots to obtain a single average spectrum. For each sample, six
259 average spectra were obtained (total of 300 shots per sample).

260 Eight different strategies for normalization of the spectra (Castro and
261 Pereira-Filho 2016, Sperança et al. 2018) were evaluated. These normalizations
262 are important to minimize the signal fluctuations (area or height) and sample
263 matrix differences during data acquisition.

264 2.5.1 Matrix-matching calibration – MMC

265 For MMC method, calibration curves in the range from 3.1 to 55 g kg⁻¹
266 Al and 0.72 to 11.6 g kg⁻¹ of Pb were obtained using four samples of waste
267 PCBs as solid standards. The curves were obtained by plotting the analytical
268 signal (y-axis emission intensity) *versus* the analyte concentration (x-axis).

269 Four emission lines with different relative intensities for Al (Al I 308.21
270 nm, Al I 309.40 nm, Al I 394.40 nm and Al I 396.15 nm) and two lines for Pb (Pb
271 I 363.95 nm e Pb I 405.78 nm) were evaluated to obtain the calibration curves.
272 The choice of the best normalization mode and the most appropriate emission
273 line was made using as a criterion the obtaining of calibration curves that

274 enable the smallest errors of prediction of the analyte concentration in the
275 samples.

276 The concentration of the analyte, using MMC, is calculated using
277 equation 1,

$$278 \quad C_{analyte} = \frac{Intensity-intercept}{slope} \quad (Eq. 1)$$

279 where $C_{analyte}$ is the concentration of Al or Pb determined in the sample,
280 Intensity is the analytical signal of the emission line obtained, slope and
281 intercept, both obtained by the calibration curve.

282 2.5.2. Two-point calibration transfer – TP CT

283 For TP CT only one sample is used as the calibration standard, and the
284 linear model is obtained with two analytical signals monitoring only one analyte
285 emission line. The linear model plot is made using two sets of spectra in the x-
286 axis, and in the y-axis the intensity of the emission line is obtained using only
287 the sum of the intensity of the spectra (height or signal area) through
288 normalization 5.

289 Using the reference concentration ($C_{standard}$) of the analyte in the
290 calibration standard, and the slopes obtained in linear models for the sample
291 ($slope_{sample}$) and for the calibration standard ($slope_{standard}$), the analyte
292 concentration ($C_{analyte}$) can be obtained using equation 2 (Castro et al. 2020).

$$293 \quad C_{analyte} = \frac{slope_{sample}}{slope_{standard}} \times C_{standard} \quad (Eq. 2)$$

294 For TP CT the emission lines Al I 396.15 nm and Pb I 405.78 nm were used to
295 obtain linear models.

296 2.5.3. One-point and multi-line calibration – OP MLC

297 For the OP MLC, only one sample is used as the calibration standard
298 and several emission lines are used to obtain calibration linear models for Al

299 and Pb. In the x-axis, the emission intensities are used for all the monitored
 300 analyte lines in the standard calibration, and in the y-axis the intensities are
 301 used for all the monitored lines in the sample.

302 The analyte concentration ($C_{analyte}$) is calculated using equation 3,

$$303 \quad C_{analyte} = slope \times C_{standard} \quad (Eq. 3)$$

304 where the slope is obtained for the linear model, and $C_{standard}$ is the
 305 concentration of the analyte in the sample used as the standard calibration (Hao
 306 et al. 2018).

307 Using four atomic emission lines for Al (308.21nm, 309.27 nm, 394.40
 308 nm and 396.15 nm) and two atomic emission lines for Pb (363.95 nm and
 309 405.78 nm), linear models were obtained for each analyte in the respective
 310 samples.

311 2.5.4. Single-sample calibration – SSC

312 In the SSC method, only one sample is used as the calibration standard
 313 and several emission lines of the analyte present in the standard and sample
 314 (unknown) are used. The SSC does not require a calibration curve or linear
 315 models (Yan et al. 2019).

316 For this strategy, the emission intensities of Al I 396.15 nm, Pb I 405.78
 317 nm and Mg II 279.55 nm were used to determine the concentration of the
 318 analyte. The S2 PCB sample containing $55 \pm 3 \text{ g kg}^{-1}$ Al, $11.6 \pm 0.8 \text{ g kg}^{-1}$ Pb
 319 and $11.4 \pm 1.8 \text{ g kg}^{-1}$ Mg (obtained after microwave digestion and ICP OES
 320 determination) was used as the calibration standard.

321 The analyte concentration ($C_{analyte}$) is calculated using equation 4,

$$322 \quad C_{analyte} = \frac{\frac{C_{standard\ analyte} \times I_{analyte\ sample}}{I_{analyte\ standard}}}{\sum_{i=1}^N \frac{C_{standard\ element}^N \times I_{element\ sample}^N}{I_{element\ standard}^N}} \quad (Eq. 4)$$

323 where $C_{\text{standard analyte}}$ and $I_{\text{analyte standard}}$ are the concentration and intensity of the
 324 emission line of the analyte in the PCB sample, respectively, used as the
 325 calibration standard (#S2 PCB). The $I_{\text{analyte sample}}$ is the emission intensity of the
 326 analyte in the unknown sample. The $I_{\text{element sample}}^N$ is the emission intensity of the
 327 element N in the sample of unknown concentration, and $C_{\text{standard element}}^N$ and $I_{\text{element standard}}^N$
 328 the concentration and the emission intensity of the element N,
 329 respectively, in the sample used as the standard calibration.

330 2.5.5. Calibration Free – CF

331 For CF only physicochemical parameters of the obtained plasma and
 332 from the monitored emission lines of the analytes and from all species present
 333 are necessary for the quantification. A calibration standard is not required.

334 The analyte concentration (C_{analyte}) is calculated using equation 5,

$$335 \ln \frac{I_{\lambda}}{A_{ki}g_k} = \ln \frac{C_{\text{analyte}}}{U(T)} - \frac{1}{K_B T} E_k \quad (\text{Eq. 5})$$

336 where I_{λ} is the integrated intensity of the emission line, A_{ki} the transition
 337 probability, g_k the degeneration of the upper level, K_B the Boltzmann constant, T
 338 the temperature of the plasma, E_k the energy level of the excited state, F the
 339 experimental factor, and $U(T)$ the partition function of the species present in the
 340 plasma (Ciucci et al. 1999, Li et al. 2019, Tognoni et al. 2010,).

341 All the calculations were processed using the LIBS++ software
 342 (ARWAN technology, developed by Palleschi et al.). For the calculation of the
 343 plasma temperature, the emission lines for Ba (Ba I 705.99, Ba II 614.17 and
 344 Ba II 649.69 nm), Fe (Fe I 374.55, Fe I 382.04, Fe I 405.58, Fe I 438.35, Fe II
 345 239.92 nm) and Ti (Ti I 498.17, Ti I 499.10 and Ti II 333.94 nm) were used.

346 The plasma electron density (N_e) was calculated from the H α line in
 347 656.28 nm and using Equation 6,

348
$$FWHA = 0.549nm \times \left(\frac{N_e}{10^{23} m^{-3}} \right)^{0.67965} \quad (\text{Eq. 6})$$

349 where FWHA denotes the full width at half area of this hydrogen emission line
350 (Cavalcante et al. 2013, Ciucci et al. 1999,).

351 Figure 1 show a pictorial description of all the calibration strategies
352 (calibration curve, linear model or correlation) used for Al.

353 2.6. Determination of analytical performance parameters

354 The precision (n=3) was calculated using all the samples. The standard
355 error (SE) and root mean square error of prediction (RMSEP) were calculated
356 for analytes, using Equations 7 and 8, respectively:

357
$$SE = \sqrt{\frac{\sum(y_i - \hat{y})^2}{n-1}} \quad (\text{Eq. 7})$$

358
$$RMSEP = \sqrt{\frac{\sum(y_i - \hat{y})^2}{n}} \quad (\text{Eq. 8})$$

359 where y_i is the analyte reference concentration obtained by ICP OES, \hat{y} is the
360 concentration predicted by the calibration model using LIBS, and n is the
361 number of samples analyzed.

362 Slope and intercept values and respective confidence interval (95 %
363 confidence level) obtained for linear regression for concentration reference (ICP
364 OES method) *versus* concentration predicted (LIBS method) plots, were used
365 for results comparison obtained in the direct determinations of analytes using
366 five calibration strategies for LIBS. The ideal situation is a slope and intercept
367 equals to 1 and 0, respectively.

368 3. Results and discussion

369 3.1. Optimization of LIBS instrumental conditions

370 The instrumental conditions of the LIBS system influence the laser-
371 matter interaction and also the quality of the emission spectrum obtained. The

372 laser pulse energy, delay time and gate width of the spectrometer were
373 optimized using a full factorial design 2^3 with center and axial points (see Table
374 S1).

375 The regression model based on the obtained OD (Table S1) was
376 calculated to determine the best description of the experimental region. The
377 quality of the model was evaluated through analysis of variance (ANOVA). After
378 observing the values calculated for ANOVA, it was possible to verify that the
379 regression of the model is not statistically significant at the 95% confidence
380 level. These results demonstrate that it is not possible to obtain a model with
381 good predictive capacity.

382 By evaluating Table S1, it was observed that experiment 8 presented
383 the highest OD value (OD = 0.89) when compared to the other experiments.
384 Thus, the evaluated conditions of this experiment were used in all
385 measurements by LIBS in this study, with a delay time of 2 μ s, a gate width of 3
386 μ s and laser pulse energy of 42.5 mJ.

387 3.2. Laser-sample interaction: energy parameters

388 The physical and chemical properties of the sample strongly influence
389 the laser-sample interaction and consequently the formation of the plasma,
390 modifying its characteristics (temperature and electronic density, among
391 others). Using SEM analysis and laser pulse energy optimized for analyses of
392 waste PCBs, some parameters were obtained from the laser-waste PCB pellet
393 interaction.

394 The crater formed by the laser pulse over the surface of the pelletized
395 waste PCB sample S2 (200 mg compressed using 10×10^4 N for 2 min) is shown
396 in Figure 2. The estimated crater diameter was 470 μ m. The figure shows the

397 heterogeneity of the morphology and composition of the sample since waste
398 PCBs consist of several polymeric, ceramic and metallic components. The
399 importance of a milling step to obtain a representative sample and thus enable
400 a stoichiometric ablation is also evident, besides the need to obtain several
401 spectra in different regions of the pelletized sample for precision in
402 determination (low RSD values). The laser-sample interaction is complex and
403 many phenomena occur as a result.

404 The irradiance ($W\text{ cm}^{-2}$) and the laser pulse fluence ($J\text{ cm}^{-2}$) were
405 calculated from the diameter of the crater. Using a laser pulse of 42.5 mJ and a
406 pulse duration of 7.7 ns, a power of 5.5 MW was generated. Even if low
407 energies are used, it is common to obtain high power values because the pulse
408 duration lasts for nanoseconds. The crater radius reached 235 μm , obtaining an
409 irradiance of 3.2 GW cm^{-2} and a laser fluence of 24.5 J cm^{-2} . These parameters
410 were calculated for the optimized instrumental conditions used to obtain all the
411 LIBS spectra for the waste PBC samples.

412 3.3. Evaluation of calibration strategies for LIBS

413 The matrix effects are the main sources of the linearity deviations
414 between concentration and emission intensity in the analysis of solids by LIBS
415 aimed at elementary determination. Thus, five calibration strategies (i- MMC, ii-
416 TP CT, iii- OP MLC, iv- SSC and v- CF) were evaluated to overcome or
417 minimize matrix effects in the determination of Al and Pb in six waste PCBs by
418 LIBS. The criterion for selecting the analytes emission lines (λ) used in each
419 calibration strategy was made considering the accuracy of the determinations
420 based on the recovery value. Recoveries values in the range of 80 to 120%
421 were considered satisfactory for all the evaluated calibration strategies.

422 Using matrix-matching calibration for Al, a calibration curve (coefficient
423 of determination: $R^2= 0.8146$) was obtained by monitoring the emission line Al I
424 396.15 nm in the following samples: S1, S2, S3 and S4. For the validation of the
425 method, two samples with intermediate concentrations to the calibration
426 standards (S5 and S6) were analyzed. Recoveries values of 99% and 116%,
427 and relative standard deviation (RSD) values $\leq 4\%$ were obtained,
428 demonstrating the satisfactory accuracy of MMC for Al determinations (see
429 Table 1).

430 For Pb, the calibration curve obtained monitoring the emission line Pb I
431 405.78 nm at samples S2, S3, S4 and S5, showed a good coefficient of
432 determination ($R^2= 0.8426$) using the MMC strategy. For samples S1 and S6
433 (used for validation), good recoveries values of 102% and 111% and RSD \leq
434 8% were obtained for Pb determinations by LIBS (see Table 2).

435 For two-point calibration transfer strategy, the S4 ($13.4 \pm 0.7 \text{ g kg}^{-1} \text{ Al}$)
436 and S1 ($7.6 \pm 0.6 \text{ g kg}^{-1} \text{ Pb}$) samples were used as calibration standards for Al
437 and Pb, respectively. Since only two calibration points ("concentrations") are
438 used, the linearity and significance of the model can be verified from the test F,
439 and in this case the ratio $F_{\text{experimental}}/F_{\text{tabulated}}$ was calculated. This ratio ≥ 10
440 demonstrated that the variances are statistically different (the quadratic mean of
441 the regression is statistically different when compared with the quadratic mean
442 of the residues), thus the model can be considered linear and statistically
443 significative, and the TP CT can be used (Pereira and Pereira-Filho 2018). The
444 ratio found for all samples analyzed for Al ranged from 7 to 416 and for Pb
445 ratios of 5 to 116 were obtained, indicating that the models are linear and that
446 two-point calibration is feasible.

447 For Al, recovery values ranging from 84 to 112% were obtained using
448 TP CT, except for S1 (683%), S2 (125%) and S3 (61%). For Pb, recovery
449 values ranging from 89 to 104% were obtained, except for sample S4 (132%)
450 (Tables 1 and 2). It was not possible to determine Pb in the S3 sample using
451 LIBS and TP CT (or any other calibration strategy evaluated), since the
452 concentration in this sample ($0.72 \pm 0.09 \text{ g kg}^{-1}\text{Pb}$) is lower than the standard
453 error (SE) calculated for the LIBS method (Table 3). RSD values $\leq 17\%$ and
454 $\leq 22\%$ were obtained in the determinations of Al and Pb, respectively, using TP
455 CT.

456 For one-point and multi-line calibration, the samples of waste PCBs
457 used as solid standards for Al and Pb were S5 ($10.2 \pm 1 \text{ g kg}^{-1} \text{ Al}$) and S2 (11.6
458 $\pm 0.8 \text{ g kg}^{-1} \text{ Pb}$), respectively. Good linear models were obtained, with excellent
459 coefficients of determination for Al (R^2 ranging from 0.9790 to 0.9960) and Pb
460 ($R^2= 1$), using four atomic emission lines for Al and two lines for Pb.

461 For Al, recoveries values ranging from 78 to 109% were obtained using
462 OP MLC, except for S3 (57%). For Pb, excellent recoveries values ranging from
463 83 to 103% were obtained for all the samples analyzed (Tables 1 and 2). The
464 values of the experimental slopes calculated for the linear models do not
465 present significant differences from the theoretical slope (see Tables 1 and 2),
466 providing good values of recoveries and demonstrating a satisfactory accuracy
467 of the determinations. RSD values $\leq 9\%$ and $\leq 25\%$ were obtained in the
468 determinations of Al and Pb, respectively.

469 Using the single-sample calibration for Al determination, the emission
470 lines and concentrations of Al and Pb for all the samples and standard were
471 used, except for samples S1 and S3. For these two samples, the intensity of the

472 emission lines of Al, Pb and Mg and the respective concentrations of these
473 elements in the calibration standard were used. Recoveries values ranging from
474 82 to 116% were obtained using SSC, except for S1 (220%).

475 However, for Pb determination the emission intensity of the Pb, Al and
476 Mg lines was used for all the waste PCB samples, together with the respective
477 concentration values of these three elements in the calibration standard, except
478 for sample S1. Only the Pb and Mg elements were monitored for this sample,
479 together with their respective concentrations in the standard for correlation with
480 the S1 sample. Recoveries values ranging from 81 to 116% were obtained
481 using SSC, except for S6 (71%) - see Table 2. Using the SSC as a calibration
482 strategy, RSD values of $\leq 21\%$ and $\leq 25\%$ were obtained in the determinations
483 of Al and Pb, respectively.

484 Calibration free was another strategy evaluated for the determination of
485 the analytes in the complex and refractory waste PCB samples. For CF it is
486 necessary to obtain some physical parameters of the plasma, such as the
487 temperature and electronic density, to verify the local thermodynamic
488 equilibrium (LTE) (Ciucci et al. 1999, Tognoni et al. 2010).

489 For the calculation of the plasma temperature using the Saha-
490 Boltzmann equation, the emission intensities of different lines in different
491 ionization states (atomic and ionic) for Ba, Fe and Ti were used. The average
492 plasma temperature was 8145 ± 227 K, considering the six waste PCB samples
493 analyzed. The physical parameters of all the elements evaluated in the CF-LIBS
494 are shown in Table S2, see supplementary material.

495 The electron density was calculated from the collision-induced
496 enlargement of the Balmer H_{α} line to the hydrogen. The average plasma

497 electron density was $0.65 \pm 0.29 \cdot 10^{17} \text{ cm}^{-3}$, considering all the samples
498 analyzed.

499 From these values obtained for the temperature and electronic density
500 of the plasma (McWhirter criterion) (Tognoni et al. 2010) it is possible to assure
501 the existence of LTE in all the samples analyzed. Thus, also taking into account
502 stoichiometric ablation and using optically thin plasma, the concentration of Al
503 and Pb in the samples can be determined.

504 For Al, excellent recovery values ranging from 90 to 106% were
505 obtained using CF for all the samples analyzed. The recovery values for Pb
506 ranged from 78 to 121%, except for S6 (162%) - see Tables 2 and 3. RSD
507 values of $\leq 26\%$ were obtained in Al and Pb determinations.

508 Some parameters related to the analytical performance and processing
509 of the data used for each of the evaluated calibration strategies are shown in
510 Table 3. It is interesting to observe how these parameters and the processing of
511 the spectra can change depending on the calibration strategy (SE and RMSEP,
512 for example). This is an indication of how matrix effects can be minimized by
513 using appropriate data processing and calibration strategies.

514 From the equations of the linear regression of the validation set (ICP
515 OES concentration reference *versus* LIBS predicted concentration plot), it is
516 possible to see that, in almost all cases the values, considering the confidence
517 interval, that the for the angular coefficient interval includes the number 1 and
518 the intercept includes the number 0, see Figures S1 and S2 in supplementary
519 material.

520 3.4. What is the best calibration strategy for the determination of Al and
521 Pb in waste PCBs by LIBS?

522 In the plasma induced by LIBS, physicochemical phenomena and
523 matrix effects occur during and due to laser-sample interaction, which in turn act
524 on the atomic emission of the analytes, directly influencing the determination of
525 Al and Pb in the samples of waste PCBs. However, with the data obtained from
526 the evaluated calibration strategies, it can be seen that some of these strategies
527 were very efficient, producing results with satisfactory accuracy. It can also be
528 seen that the intrinsic properties of each analyte and of each calibration strategy
529 directly influence the choice of the best calibration strategy.

530 The matrix-matching calibration gave excellent results for the
531 determination of both analytes, with satisfactory recovery and RSD values. The
532 MMC proved to be an efficient calibration strategy for the analysis of solids by
533 LIBS, because since a set of waste PCB samples were used as calibration
534 standards, the possible matrix effects are minimized when the physical
535 properties of the calibration standards are close to those of the analyzed
536 samples.

537 One limitation of the use of MMC in this study is that there is no set of
538 certified reference materials (CRM) of waste PCBs, with reference values for Al
539 and Pb, which could be used as solid standards when obtaining the calibration
540 curve. Few initiatives are observed in the literature in order to produce a
541 reference material for WEEE and a good example was published by Andrade et
542 al. 2019a, 2019c. Thus, it was necessary to first obtain reference values of the
543 analytes by analyzing a set of samples by a reference technique (in this study
544 an ICP OES was used) for use as calibration standards for the LIBS method.

545 In some cases it is necessary to use vigorous conditions for the
546 decomposition of the samples (high temperatures and high volume of

547 concentrated acid, as in this study). This represents a limitation in the use of
548 MMC in the absence of adequate sample preparation instruments and
549 reference values of the analytes required for later use of the samples as solid
550 calibration standards for LIBS.

551 Two-point calibration transfer requires only one calibration standard
552 (CRM or one reference value sample) and one sample with unknown
553 concentration to determine the analyte concentration. In this calibration
554 strategy, each set of spectra obtained in the LIBS analysis for standard and
555 sample are divided into two sets and subsequently summed (the number of
556 spectra composing set 2 must have approximately two-fold the number of
557 spectra of set 1) (Castro et al. 2020).

558 If the standard and the sample have similar physical properties (for
559 efficient matrix-matching), and the concentration of the standard is close to that
560 of the sample, TP CT minimizes the matrix effects and enables a high degree of
561 accuracy when determining the analyte concentration in the sample, using only
562 one calibration standard and one linear model with two points. Tables 1 and 2
563 show that good recoveries values (ranging from 80 to 120%) were obtained for
564 Al and Pb, when the concentration of the standard used was close to the
565 concentration of these analytes in the sample. For samples with concentrations
566 very different from those of the standards used, there was an under- or over-
567 estimation of the analyte concentration.

568 The TP CT is an interesting simple calibration strategy for LIBS analysis
569 when there is not a great variability of analyte concentration in the analyzed
570 samples and when a standard with an appropriate concentration similar to that
571 of the samples is used. This situation can be achieved in routine analysis.

572 Another strategy evaluated was one-point and multi-line calibration - OP
573 MLC. Excellent results were obtained for all the determinations of Al (except for
574 sample S3) and Pb in the waste PCB samples by LIBS. The OP MLC requires
575 only one calibration standard and several lines of analyte emission to obtain the
576 linear model, which facilitates the implementation of this calibration strategy
577 when few solid calibration standards are available in the laboratory routine.
578 Extra care has to be taken when using the OP MLC to remove lines with low
579 intensity that present spectral interferences, since they can harm the linear
580 models and consequently the measurement accuracy (Hao et al. 2018).

581 The determination of Al and Pb was also evaluated using the single-
582 sample calibration method - SSC, which is another recent calibration strategy
583 for LIBS that uses only one sample as standard (reference). In this strategy, a
584 simple correlation calculation is necessary to determine the analyte
585 concentration in the sample with unknown concentration (Yan et al. 2019).
586 Using SSC, good recoveries values were obtained for both Al (except sample
587 S1) and Pb (except sample S6).

588 For the use of SSC, the extent of the matrix effects between the sample
589 and the standard should be considered the same for all elements present in the
590 LIBS-induced plasma sample and the standard, since a direct correlation
591 between the emission intensity and concentration of these elements will be
592 used for the determination of the analyte. In addition, it should be considered
593 that none of the emission lines used in the SSC (analyte emission lines and
594 other elements used in the correlation) present spectral interferences, so that
595 results can be obtained with satisfactory precision and recovery (Yan et al.
596 2019).

597 Finally, using calibration free (CF) it was possible to obtain good results
598 with excellent accuracy for Al and Pb determinations, except for Al
599 determination in sample S6, using direct analysis of waste PCB samples by
600 LIBS.

601 Not requiring a calibration standard is an advantage of CF, which
602 makes it an excellent calibration strategy for use in elemental determination by
603 LIBS in complex samples difficult to decompose. However, the quality of data
604 acquisition and treatment in CF is a critical factor for obtaining satisfactory
605 results. It is necessary to ensure that the emission measurements are obtained
606 in LTE in the plasma, that the physical parameters used are correctly obtained
607 and calculated with precision, and that only emission lines free of spectral
608 interferences and self-absorption are employed in CF. Despite it is a laborious
609 calculation procedure, CF allows the achievement of good results.

610 In this context, it is evident that it is difficult to choose the best
611 calibration strategy for the direct determination of Al and Pb in waste PCBs by
612 LIBS, since it depends on many variables. However, a knowledge of the
613 advantages and limitations of each calibration strategy and a consideration of
614 some intrinsic characteristics (physicochemical properties) of the sample and
615 the analytes can help in selecting the best strategy that efficiently overcomes
616 matrix effects and enables determination with satisfactory accuracy.

617 Table 4 shows some characteristics, advantages and limitations of the
618 five calibration strategies evaluated in this study. This may help the reader to
619 choose and evaluate the best calibration strategy for LIBS that could be used in
620 different analytical contexts.

621 It is worth noting that there seems to be a tendency in recently reported
622 new calibration strategies for LIBS to use no or few calibration standards (only 1
623 or 2) and to increasingly explore the physicochemical parameters and
624 correlations of concentrations of the species present in the plasma induced by
625 laser in each sample analyzed. Examples are TP CT, OP MLC, SSC evaluated
626 in this study and other strategies recently reported in the scientific literature
627 such as MEC (Babos et al. 2018) and OP GSA (Babos et al. 2019, Castro et al.
628 2020) calibration.

629 3.5 Evaluation of Al and Pb concentrations in waste PCBs: economic
630 and environmental questions

631 As mentioned previously, waste PCBs can contain high concentrations
632 of valuable and toxic metals. The recycling and appropriate disposal of this
633 waste can both provide a source of income and contribute to environmental
634 protection. In this context, LIBS is an excellent analytical tool for the monitoring
635 of metals in the waste and for the development of methods for the analysis of
636 solids and the direct determination of Al and Pb present in PCBs.

637 Were calculated estimations of the commercial value (in US\$) per ton of
638 each of the six samples of waste PCBs analyzed, considering only the
639 measured concentrations of Al (ranging from 3.1 to 55 g kg⁻¹ Al) and Pb
640 (ranging from 0.72 to 11.6 g kg⁻¹ Pb). Considered the prices of 1803 US\$/tonne
641 Al and 1919 US\$/tonne Pb quoted on the London Metal Exchange, the second
642 world center for industrial metals trading (LME, 2019).

643 The commercial value per tonne of the analyzed samples, considering
644 only the Al and Pb contents, range from 20 to 121 US\$/tonne of waste PCB
645 (prices for the S1 and S2 samples, respectively). These are good prices for

646 samples that are considered waste, particularly as they apply only to two metals
647 present in the waste. Other valuable metals may also be present and thus the
648 market price per ton of waste PCBs may be higher.

649 Concerning the environmental question, only one sample (S3 PCB,
650 0.072% Pb) complies with the maximum concentration value allowed (0.1% Pb)
651 by weight in homogeneous materials for Pb in WEEE under Directive
652 2011/65/EU (RoHS, 2011). The Pb concentration in the other samples is
653 between 5 and 12 times above the maximum allowed value according to the
654 normative instruction. This is worrying, since if these samples are
655 inappropriately disposed of they may be a source of contamination in the
656 environment because of the Pb metal content.

657

658 **Conclusion**

659 The choice of the best calibration strategy for the direct analysis of waste PCBs
660 for LIBS when aiming to determine Al and Pb depends on the intrinsic
661 properties of these analytes and samples, as well as the ability of each of the
662 calibration strategies to overcome the various matrix effects. Of the five
663 calibration strategies evaluated, MMC and CF generally allowed accurate
664 values to be obtained for both analytes in all the samples. The LIBS technique
665 presented itself as an excellent analytical tool in the fast, simple and direct
666 monitoring of recyclable metals such as Al and Pb and also of potential for
667 environmental contamination such as Pb, originating from WEEE (waste PCB).
668 The Pb concentrations determined are of concern as only one sample was in
669 accordance with the Directive 2011/65/EU.

670

671 **Credit author statement**

672 Diego Victor Babos: Conceptualization; Data curation; Formal analysis;
673 Validation; Visualization; Roles/Writing - original draft; Writing - review & editing.

674 Andrés Cruz-Conesa: Conceptualization; Data curation; Formal analysis;
675 Validation; Visualization; Roles/Writing - original draft; Writing - review & editing.

676 Edenir Rodrigues Pereira-Filho: Conceptualization; Formal analysis; Resources;
677 Supervision; Visualization; Writing - review & editing.

678 Jesús Manuel Anzano: Formal analysis; Funding acquisition; Project
679 administration; Resources; Supervision; Visualization; Writing - review & editing.

680 **Declaration of Competing Interest**

681 The authors declare that they have no known competing financial
682 interests or personal relationships that could have appeared to influence the
683 work reported in this paper.

684 **Acknowledgements**

685 The authors are grateful to the Conselho Nacional de Desenvolvimento
686 Científico e Tecnológico (CNPq – grants 141311/2017-7, 305637/2015-0) for
687 fellowships and financial support. This study was financed in part by the
688 Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil
689 (CAPES) - Finance Code 001, the Government of Aragon, the Servicio General
690 de Apoyo a la Investigación-SAI, UNIZAR & the European Base Found,
691 proposal E23_17D, and the Spanish Ministry of Science and Innovation,
692 proposal #CTM2017-82929-R. The authors are also grateful to the São Paulo
693 Research Foundation (FAPESP, grants 2016/01513-0). We would like to thank

694 MSc. Daniel F. Andrade and Dr. Raquel C. Machado for donating the electronic
695 waste reference material.

696

697 **References**

698

699 Andrade, D.F., Machado, R.C., Pereira-Filho, E.R., 2019a. Proposition of
700 electronic waste as a reference material – part 2: homogeneity, stability,
701 characterization, and uncertainties J. Anal. At. Spectrom. 34, 2402-2410.
702 <https://doi.org/10.1039/C9JA00284G>

703 Andrade, D.F., Fortunato, F.M., Pereira-Filho, E.R., 2019b. Calibration
704 strategies for determination of the In content in discarded liquid crystal
705 displays (LCD) from mobile phones using laser-induced breakdown
706 spectroscopy (LIBS). Anal. Chim. Acta 1061, 42-49.
707 <https://doi.org/10.1016/j.aca.2019.02.038>

708 Andrade, D.F., Machado, R.C., Bacchi, M., Pereira-Filho, E.R., 2019c.
709 Proposition of electronic waste as a reference material – part 1: sample
710 preparation, characterization and chemometric evaluation. J. Anal. At.
711 Spectrom. 34, 2394-2401. <https://doi.org/10.1039/C9JA00283A>

712 Andrade, D.F., Romanelli J.P., Pereira-Filho, E.R., 2019d. Past and emerging
713 topics related to electronic waste management: top countries, trends,
714 and perspectives. Environ. Sci. Pollut. Res. 26, 17135-17151.
715 <https://doi.org/10.1007/s11356-019-05089-y>

716 Andrade, D.F., Pereira-Filho, E.R., Amarasiriwardena, D., 2020. Current trends
717 in laser-induced breakdown spectroscopy: a tutorial review. Appl.
718 Spectrosc. Rev., <https://doi.org/10.1080/05704928.2020.1739063>

719 Aquino, F.W.B., Paranhos, C.M., Pereira-Filho, E.R., 2016. Method for the
720 production of acrylonitrile–butadiene–styrene (ABS) and polycarbonate
721 (PC)/ABS standards for direct Sb determination in plastics from e-waste
722 using laser-induced breakdown spectroscopy. J. Anal. At. Spectrom. 31,
723 1228-1233. <https://doi.org/10.1039/C6JA00038J>

724 Arshadi, M., Yaghmaei, S., Mousavi, S.M., 2018. Recycling organics from non-
725 metallic fraction of waste printed circuit boards by a novel conical
726 surface triboelectric separator. Resour. Conserv. Recy. 139, 298-306.
727 <https://doi.org/10.1016/j.resconrec.2018.08.013>

728 Augusto, A.S., Castro, J.P., Sperança, M.A., Pereira-Filho, E.R.,
729 2019. Combination of Multi-Energy Calibration (MEC) and Laser-
730 Induced Breakdown Spectroscopy (LIBS) for Dietary Supplements
731 Analysis and Determination of Ca, Mg and K. J. Braz. Chem. Soc. 30,
732 804-812. <https://doi.org/10.21577/0103-5053.20180211>.

733 Babos, D.V., Barros, A.I., Nóbrega, J.A., Pereira-Filho, E.R., 2019. Calibration
734 strategies to overcome matrix effects in laser-induced breakdown
735 spectroscopy: Direct calcium and phosphorus determination in solid
736 mineral supplements. *Spectrochim. Acta B* 155, 90-98.
737 <https://doi.org/10.1016/j.sab.2019.03.010>

738 Babos, D.V., Virgilio, A., Costa, V.C., Donati, G.L., Pereira-Filho, E.R., 2018.
739 Multi-energy calibration (MEC) applied to laser-induced breakdown
740 spectroscopy (LIBS). *J. Anal. At. Spectrom.* 33, 1753-1762.
741 <https://doi.org/10.1039/C8JA00109J>

742 Baldé, C., Forti, V., Gray, V., Kuehr, R., Stegmann, P., *The Global E-waste
743 Monitor 2017: Quantities, Flows, and Resources.* 2017.

744 Carvalho, A.A.C., Cozer, L.A., Luz, M.S., Nunes, L.C., Rocha, F.R.P., Nomura,
745 C.S., 2019. Multi-energy calibration and sample fusion as alternatives for
746 quantitative analysis of high silicon content samples by laser-induced
747 breakdown spectrometry. *J. Anal. At. Spectrom.* 34, 1701-1707.
748 <https://doi.org/10.1039/C9JA00149B>

749 Carvalho, G.G.A., Guerra, M.B.B., Adame, A., Nomura, C.S., Oliveira, P.V.,
750 Carvalho, H.W.P., Santos Jr, D., Nunes L.C., Krug, F.J., 2018a.
751 Recent advances in LIBS and XRF for the analysis of plants. *J. Anal. At.
752 Spectrom.* 33, 919-944. <https://doi.org/10.1039/C7JA00293A>

753 Carvalho, A.A.C., Leme, F.O., Luz, M.S., Oliveira, P.V., Nomura, C.S., 2018b.
754 Internal standard fused glass beads for high silicon content sample analysis
755 by laser-induced breakdown spectrometry. *J. Anal. At. Spectrom.* 33,
756 1243-1250. <https://doi.org/10.1039/C8JA00112J>

757 Carvalho, R.R.V., Coelho, J.A.O., Santos, J.M., Aquino, F.W.B., Carneiro,
758 R.L., Pereira-Filho, E.R., 2015. Laser-induced breakdown
759 spectroscopy (LIBS) combined with hyperspectral imaging for the
760 evaluation of printed circuit board composition. *Talanta* 134, 278-283.
761 <https://doi.org/10.1016/j.talanta.2014.11.019>

762 Castro, J.P., Babos, D.V., Pereira-Filho, E.R., 2020. Calibration strategies for
763 the direct determination of rare earth elements in hard disk magnets
764 using laser-induced breakdown spectroscopy. *Talanta* 208, 120443.
765 <https://doi.org/10.1016/j.talanta.2019.120443>

766 Castro, J.P., Pereira-Filho, E. R., 2016. Twelve different types of data
767 normalization for the proposition of classification, univariate and multivariate
768 regression models for the direct analyses of alloys by laser-induced
769 breakdown spectroscopy (LIBS). *J. Anal. At. Spectrom.* 31, 2005-2014.
770 <https://doi.org/10.1039/C6JA00224B>

771 Cavalcanti, G.H., Teixeira, D.V., Legnaioli, S., Lorenzetti, G., Pardini, L.,
772 Palleschi, V., 2013. One-point calibration for calibration-free laser-
773 induced breakdown spectroscopy quantitative analysis. *Spectrochim.*
774 *Acta B* 87, 51-56. <http://dx.doi.org/10.1016/j.sab.2013.05.016>

775 Ciucci, A., Corsi, M., Palleschi, V., Rastelli, S., Salvetti, A., Tognoni, E., 1999.
776 New Procedure for Quantitative Elemental Analysis by Laser-Induced
777 Plasma Spectroscopy. *Appl. Spectrosc.* 53, 960-964.
778 <https://www.osapublishing.org/as/abstract.cfm?URI=as-53-8-960>

779 Costa, V.C., Castro, J.P., Andrade, D.F., Babos, D.V., Garcia, J.A., Sperança,
780 M.A., Catelani, T.A., Pereira-Filho, E.R., 2018a. Laser-induced
781 breakdown spectroscopy (LIBS) applications in the chemical analysis
782 of waste electrical and electronic equipment (WEEE). *Trends Anal.*
783 *Chem.* 108, 65-73. <https://doi.org/10.1016/j.trac.2018.08.003>

784 Costa, V.C., Augusto, A.S., Castro, J.P., Machado, R.C., Andrade, D.F., Babos,
785 D.V., Sperança, M.A., Gamela, R.R., Pereira-Filho, E.R., 2019. laser
786 induced-breakdown spectroscopy (LIBS): history, fundamentals,
787 applications and potentialities. *Quim. Nova* 42, 527-545.
788 <http://dx.doi.org/10.21577/0100-4042.20170325>

789 Costa, V.C., Babos, D.V., Aquino, F.W.B., Virgilio, A., Amorim, F.A.C., Pereira-
790 Filho, E.R., 2018b. Direct Determination of Ca, K and Mg in Cassava
791 Flour Samples by Laser-Induced Breakdown Spectroscopy (LIBS).
792 *Food Anal. Methods* 11, 1886-1896. [https://doi.org/10.1007/s12161-](https://doi.org/10.1007/s12161-017-1086-9)
793 [017-1086-9](https://doi.org/10.1007/s12161-017-1086-9)

794 Cremers, D.A., Radziemski, L.J., *Handbook of laser-induced breakdown*
795 *spectroscopy*, Wiley, London, 2006a.

796 Cremers D. A., Radziemski, L. J., History and fundamentals of LIBS, in:
797 Miziolek, A.W., Palleschi, V., Schechter, I., (Eds.), *Laser-Induced*
798 *Breakdown Spectroscopy*, Cambridge University Press, New York,
799 2006b

800 Derringer, G., Suich, R., 1980. Simultaneous Optimization of Several Response
801 Variables. *J. Qual. Technol.* 12, 214-219.
802 <https://doi.org/10.1080/00224065.1980.11980968>

803 Eppler, A.S., Cremers, D.A., Hickmott, D.D., Ferris, M.J., Koskelo, A.C., 1996.
804 Matrix Effects in the Detection of Pb and Ba in Soils Using Laser-
805 Induced Breakdown Spectroscopy. *Appl. Spectrosc.* 50, 1175-1181.
806 <https://doi.org/10.1366/0003702963905123>

807 Fortunato, F.M., Catelani, T.A., Pomares-Alfonso, M.S., Pereira-Filho, E.R.,
808 2019. Application of Multi-energy Calibration for Determination of
809 Chromium and Nickel in Nickeliferous Ores by Laser-induced
810 Breakdown Spectroscopy. *Anal. Sci.* 35, 165-168.
811 <https://doi.org/10.2116/analsci.18P286>

- 812 Gomes, M.S., de Carvalho, G.G.A., Junior, D.S., Krug, F.J., 2013. A novel
813 strategy for preparing calibration standards for the analysis of plant
814 materials by laser-induced breakdown spectroscopy: A case study
815 with pellets of sugar cane leaves. *Spectrochim. Acta B* 86, 137-141.
816 <https://doi.org/10.1016/j.sab.2013.03.009>
- 817 Gondal M.A., Seddigi, Z.S., Nasr, M.M., Gondal, B., 2010. Spectroscopy
818 detection of health hazardous contaminants in lipstick using Laser
819 induced breakdown spectroscopy, *J. Hazard Mater.* 175, 726-732.
820 <https://doi.org/10.1016/j.jhazmat.2009.10.069>
- 821 Hahn, D.W., Omenetto, N., 2010. Laser-Induced Breakdown Spectroscopy
822 (LIBS), Part I: Review of Basic Diagnostics and Plasma-Particle
823 Interactions: Still-Challenging Issues within the Analytical Plasma
824 Community. *Appl. Spectrosc.*, 2010, 64, 335-366.
825 <https://doi.org/10.1366/000370210793561691>
- 826 Hahn, D.W., Omenetto, N., 2012. Laser-Induced Breakdown Spectroscopy
827 (LIBS), Part II: Review of Instrumental and Methodological
828 Approaches to Material Analysis and Applications to Different Fields.
829 *Appl. Spectrosc.* 66, 347-419. <https://doi.org/10.1366/11-06574>
- 830 Hao, Z.Q., Liu, L., Zhou, R., Ma, Y.W., Li, X.Y., Guo, L.B., Lu, Y.F., Zeng, X.Y.,
831 2018. One-point and multi-line calibration method in laser-induced
832 breakdown spectroscopy. *Opt. Express* 26, 22926-22933.
833 <https://doi.org/10.1364/OE.26.022926>
- 834 Kim, G., Kwak, J., Kim, K.R., Lee, H., Kim, K.W., Yang, H., Park, K., 2013.
835 Rapid detection of soils contaminated with heavy metals and oils
836 by laser induced breakdown spectroscopy (LIBS), *J. Hazard Mater.*
837 263, 754-760. <http://dx.doi.org/10.1016/j.jhazmat.2013.10.041>
- 838 Lasheras, R.J., Bello-Gálvez, C., Anzano, J. M., 2013. Quantitative analysis of
839 oxide materials by laser-induced breakdown spectroscopy with argon
840 as an internal standard. *Spectrochim. Acta B* 82, 65-70.
841 <https://doi.org/10.1016/j.sab.2013.01.005>
- 842 Lasheras, R.J., Bello-Gálvez, C., Rodríguez-Celis, E.M., Anzano, J., 2011.
843 Discrimination of organic solid materials by LIBS using methods of
844 correlation and normalized coordinates, *J. Hazard Mater.* 192, 704-
845 713. <https://doi.org/10.1016/j.jhazmat.2011.05.074>
- 846 Lednev, V. N., Grishin, M.Y., Sdvizhenskii, P.A., Asyutin, R.D., Tretyakov, R. S.,
847 Stavertiy, A.Ya., Pershin, S. M., 2019. Sample temperature effect on
848 laser ablation and analytical capabilities of laser induced breakdown
849 spectroscopy. *J. Anal. At. Spectrom.* 34, 607-615.
850 <https://doi.org/10.1039/C8JA00348C>
- 851 Li, T., Hou, Z., Fu, Y., Yu, J., Gu, W., Wang, Z., 2019. Correction of self-
852 absorption effect in calibration-free laser-induced breakdown
853 spectroscopy (CF-LIBS) with blackbody radiation reference. *Anal.*
854 *Chim. Acta* 1058, 39-47. <https://doi.org/10.1016/j.aca.2019.01.016>
- 855 London Metal Exchange - LME. <https://www.lme.com/>, 2019

856 Miziolek, W., Palleschi, V., Schechter, I., Laser induced breakdown
857 spectroscopy. Cambridge University Press, Cambridge, 2006.

858 Morais, C.P., Barros, A.I., Bechlin, M.A., Silva, T.V., Santos Júnior, D.,
859 Senesi, G.S., Crespi, M.S., Ribeiro, C.A., Gomes Neto, J. A.,
860 Ferreira, E. C., 2018. Laser-induced breakdown spectroscopy
861 determination of K in biochar-based fertilizers in the presence of easily
862 ionizable element. *Talanta*, 188, 199-202.
863 <https://doi.org/10.1016/j.talanta.2018.05.089>

864 NIST electronic database, <https://www.nist.gov/pml/atomic-spectra-database>

865 Pereira, F.M.V., Pereira-Filho., E.R., 2018. Application of free computational
866 program in experimental design: a tutorial. *Quim. Nova* 41, 1061-1071.
867 <http://dx.doi.org/10.21577/0100-4042.20170254>

868 Perkins, D.N., Drisse, M.-N.B., Nxele, T., Sly, P.D., 2014. E-Waste: A Global
869 Hazard. *Ann. Glob. Health* 80, 286-295.
870 <http://doi.org/10.1016/j.aogh.2014.10.001>

871 Popov, A.M., Zaytsev, S.M., Seliverstova, I.V., Zakuskin, A.S., Labutin, T.A.,
872 2018. Matrix effects on laser-induced plasma parameters for soils and
873 ores. *Spectrochim. Acta B* 148, 205-210.
874 <https://doi.org/10.1016/j.sab.2018.07.005>

875 Restriction of Hazardous Substances Directive (RoHS) Directive 2011/65/EU
876 Restriction of the Use of Certain Hazardous Substances in Electrical
877 and Electronic Equipment, The European Parliament and the Council
878 of the E. Union, 2011. <http://data.europa.eu/eli/dir/2011/65/oj>

879 Rezaei, A.H., Keshavarz, M.H., Tehrani, M.K., Darbani, S.M.R., 2018.
880 Quantitative analysis for the determination of aluminum percentage
881 and detonation performance of aluminized plastic bonded
882 explosives by laser-induced breakdown spectroscopy. *Laser Phys.*
883 28, 065605. <https://doi.org/10.1088/1555-6611/aab660>

884 Sattar, H., Sun, L., Imran, M., Hai, R., Wu, D., Ding, H., 2019. Effect of
885 parameter setting and spectral normalization approach on study of
886 matrix effect by laser induced breakdown spectroscopy of Ag–Zn
887 binary composites. *Plasma Sci. Technol.* 21, 034019
888 <https://doi.org/10.1088/2058-6272/aaf712>

889 Sperança, M.A., Andrade, D.F., Castro, J. P., Pereira-Filho, E.R., 2019. Univariate
890 and multivariate calibration strategies in combination with laser-
891 induced breakdown spectroscopy (LIBS) to determine Ti on
892 sunscreen: A different sample preparation procedure. *Opt. Laser
893 Technol.* 109, 648-653. <https://doi.org/10.1016/j.optlastec.2018.08.056>

894 Sperança, M.A., Pomares-Afonso, M.S., Pereira-Filho, E.R., 2018. Analysis of
895 Cuban nickeliferous minerals by laser-induced breakdown spectroscopy
896 (LIBS): non-conventional sample preparation of powder samples. *Anal.
897 Methods*.10, 533-540. <https://doi.org/10.1039/C7AY02521A>

- 898 Takahashi, T., Thornton, B., 2017. Quantitative methods for compensation of
899 matrix effects and self-absorption in Laser Induced Breakdown
900 Spectroscopy signals of solids. *Spectrochim. Acta B* 138, 31-42.
901 <https://doi.org/10.1016/j.sab.2017.09.010>
- 902 Tansel, B., 2017. From electronic consumer products to e-wastes: Global
903 outlook, waste quantities, recycling challenges. *Environ. Int.* 98, 35-45.
904 <https://doi.org/10.1016/j.envint.2016.10.002>
- 905 Tognoni, E., Cristoforetti, G., Legnaioli, S., Palleschi, V., 2010. Calibration-Free
906 Laser-Induced Breakdown Spectroscopy: State of the art.
907 *Spectrochim. Acta B* 65, 1-14. doi:10.1016/j.sab.2009.11.006
- 908 Vieira, A.L., Silva, T.V., de Sousa, F.S.I., Senesi, G.S., Santos Júnior, D.,
909 Ferreira, E. C., Gomes Neto, J. A., 2018. Determinations of
910 phosphorus in fertilizers by spark discharge-assisted laser-induced
911 breakdown spectroscopy. *Microchem. J.* 139, 322-326.
912 <https://doi.org/10.1016/j.microc.2018.03.011>
- 913 Wu, C., Sun, D.X., Su, M.G., Yin, Y.P., Han, W.W., Lu, Q.F., Dong, C.Z., 2019.
914 Quantitative analysis of Pb in soil samples by laser-induced
915 breakdown spectroscopy with a simplified standard addition method. *J.*
916 *Anal. At. Spectrom.* 34, 1478-1484. DOI: 10.1039/c9ja00059c
- 917 Yamane, L.H., de Moraes, V.T., Espinosa, D.C.R., Tenório, J.A.S., 2011.
918 Recycling of WEEE: Characterization of spent printed circuit boards
919 from mobile phones and computers. *Waste Manage.* 31, 2553-2558.
920 <https://doi.org/10.1016/j.wasman.2011.07.006>
- 921 Yan, R., Tang, Y., Zhu, Z., Hao, Z., Li, J., Yu, H., Yu, Y., Guo, L., Zeng, X., Lu,
922 Y., 2019. Accuracy improvement of quantitative analysis for major
923 elements in laser-induced breakdown spectroscopy using single-
924 sample calibration. *Anal. Chim. Acta* 1064, 11-16.
925 <https://doi.org/10.1016/j.aca.2019.02.056>
- 926 Yang, J., Wang, H., Zhang, G., Bai, X., Zhao, X., He, Y., 2019. Recycling
927 organics from non-metallic fraction of waste printed circuit boards by a
928 novel conical surface triboelectric separator. *Resour. Conserv. Recy.*
929 146, 264-269. <https://doi.org/10.1016/j.resconrec.2019.03.008>
- 930 Yi, R.X., Guo, L.B., Zou, X.H., Li, J.M., Hao, Z.Q., Yang, X. Y., Li, X.Y., Zeng,
931 X.Y., Lu, Y.F., 2016. Background removal in soil analysis using laser-
932 induced breakdown spectroscopy combined with standard addition
933 method. *Opt. Express* 24, 2607-2618.
934 <https://doi.org/10.1364/OE.24.002607>

Table captions

Table 1. Concentrations (mean \pm standard deviation, g kg⁻¹ Al, n=3) and recovery (%) for Al in PCB samples determined by LIBS using matrix-matching calibration (MMC), two-point calibration transfer (TP CT), one-point and multi-line calibration (OP MLC), single-sample calibration (SSC) and calibration free (CF).

Sample	ICP OES	MMC	TP CT	OP MLC		SSC	CF	
		g kg ⁻¹		Theoretical slope*	Experimental Slope	g kg ⁻¹		
S1	3.1 \pm 0.4	-	21.2 \pm 3.6 (683)	0.30	0.28 \pm 0.03	2.9 \pm 0.3 (93)	6.8 \pm 1.1 (220)	3.3 \pm 0.1 (106)
S2	55 \pm 3	-	68.9 \pm 8.4 (125)	5.39	5.87 \pm 0.11	59.8 \pm 1 (109)	-	49.8 \pm 9.2 (91)
S3	21.4 \pm 0.6	-	13.0 \pm 1.4 (61)	2.09	1.19 \pm 0.07	12.1 \pm 0.6 (57)	24.8 \pm 5.1 (116)	21.4 \pm 3.1 (100)
S4	13.4 \pm 0.7	-	-	1.32	1.02 \pm 0.08	10.4 \pm 0.8 (78)	13.5 \pm 1.4 (101)	13.1 \pm 3.4 (98)
S5	10.2 \pm 1	11.8 \pm 0.1 (116)	11.4 \pm 0.9 (112)	-	-	-	10.4 \pm 2.1 (102)	10.0 \pm 2 (98)
S6	15.2 \pm 0.9	15.0 \pm 0.5 (99)	12.7 \pm 1.4 (84)	1.49	1.23 \pm 0.05	12.6 \pm 0.5 (83)	12.4 \pm 0.6 (82)	13.6 \pm 1.2 (90)

- : Samples used for calibration

*Theoretical slope: $slope = \frac{C_{analyte}}{C_{standard}}$

Table 2. Concentrations (mean \pm standard deviation, g kg⁻¹ Pb, n=3) and recovery (%) for Pb in PCB samples determined by LIBS using matrix-matching calibration (MMC), two-point calibration transfer (TP CT), one-point and multi-line calibration (OP MLC), single-sample calibration (SSC) and calibration free (CF).

Sample	ICP OES	MMC	TP CT	OP MLC		SSC	CF	
		g kg ⁻¹		Theoretical slope*	Experimental Slope	g kg ⁻¹		
S1	7.6 \pm 0.6	7.8 \pm 0.5 (102)	-	0.655	0.574 \pm 0.089	6.7 \pm 1 (88)	7.3 \pm 0.6 (96)	5.9 \pm 0.6 (78)
S2	11.6 \pm 0.8	-	11.6 \pm 0.8 (100)	-	-	-	-	14.1 \pm 3.6 (121)
S3	0.72 \pm 0.09	-	<1.1	0.062	0.008 \pm 0.002	<1.2	<1.7	<2.7
S4	4.7 \pm 0.9	-	6.2 \pm 0.1 (132)	0.405	0.413 \pm 0.029	4.8 \pm 0.3 (103)	5.4 \pm 0.3 (116)	5.5 \pm 0.8 (116)
S5	10.7 \pm 0.6	-	9.5 \pm 2.1 (89)	0.922	0.766 \pm 0.059	8.9 \pm 0.7 (83)	8.6 \pm 2.1 (81)	10.3 \pm 2.2 (97)
S6	6.9 \pm 1.6	7.6 \pm 0.6 (111)	7.2 \pm 0.9 (104)	0.595	0.611 \pm 0.160	7.1 \pm 1.8 (103)	4.9 \pm 0.8 (71)	11.2 \pm 2.2 (162)

- : Samples used for calibration

*Theoretical slope: $slope = \frac{C_{analyte}}{C_{standard}}$

Table 3. Analytical performance parameters

Parameter	Matrix-matching calibration	Two-point calibration transfer	Calibration free	One point and multi-line calibration		Single-sample calibration
Emission line (nm)	Al I 396.15 Pb I 405.78	Al I 396.15 Pb I 405.78	Several lines*	Al I 308.21 Al I 309.27 Al I 394.40 Al I 396.15	Pb I 363.95 Pb I 405.78	Al I 396.15 Pb I 405.78 Mg II 279.55
Normalization selected						
Al	Each individual spectrum is divided by its Euclidean norm and the average is calculated	Sum	Average of the spectra	Each individual spectrum is divided by its Euclidean norm, and the average is calculated		Each individual spectrum is divided by its Euclidean norm and the average is calculated
Pb	Average of the spectra	Sum	Average of the spectra	Average of the spectra		Average of the spectra
Signal type						
Al	Height	Height	Area	Height		Area
Pb	Height	Height	Area	Area		Height
SE (g kg ⁻¹)						
Al	1.6	12.2	2.4	5.6		2.9
Pb	0.76	1.1	2.7	1.2		1.7
RMSEP (g kg ⁻¹)						
Al	1.1	10.9	2.2	5.0		2.6
Pb	0.49	0.87	2.4	0.91		1.3
RSD range (%)						
Al	1 - 4	8 - 17	3 - 26	2 - 9		5 - 21
Pb	6 - 8	2 - 22	10 - 26	6 - 25		6 - 25

* see Table S2 in Electronic Supplementary Information (ESI).

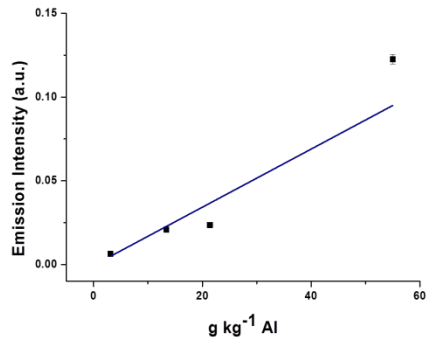
Table 4. Advantages and limitations of the calibration strategies evaluated in this study for the determination of Al and Pb in waste PCBs by LIBS.

Calibration Method	Number of emission lines	Number of reference standard	Advantages	Limitations	Reference
Matrix-matching calibration	One	Between four and five	Efficient matching of the physical properties of the calibration standards with the samples	Difficulty in obtaining a set of commercial CRM or samples with reference values	Vieira et al. 2018, this study
Calibration free	Several	Not necessary	Does not require the use of calibration curves or matrix-matched standards	Occurrences of lines with self-absorption and spectral interferences, which compromise the determinations, laborious calculations	Tognoni et al. 2010, this study
One point and multi-line calibration	Several	One	Requires only one calibration standard	The choice of the standard with appropriate concentration, and the use of emission lines with low sensitivities	Hao et al. 2018, this study
Two-point calibration transfer	One	One	Simplicity in data processing and measurement accuracy	The choice of the standard with appropriate concentration as samples, and standards should show little variability between analyte concentrations	Castro et al. 2020, this study
Single-sample calibration	The number of lines of analytes present in the sample shall be \leq to the number of lines used of the elements in the standard	One	No calibration curve or linear calibration model required	Samples and standards with significant variability of physico-chemical properties and analyte emission lines and reference elements with spectral interferences	Yan et al. 2019, this study

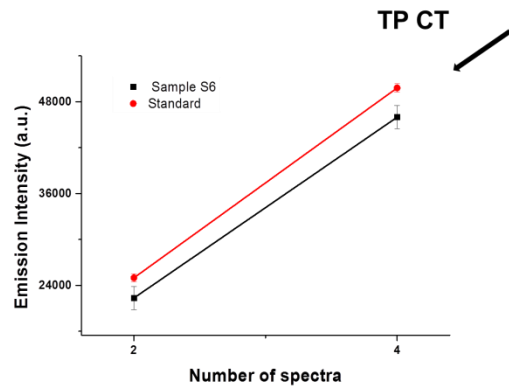
Figure captions

Figure 1. Scheme representation of the calibration strategies evaluated for direct determination of Al in waste PCBs by LIBS.

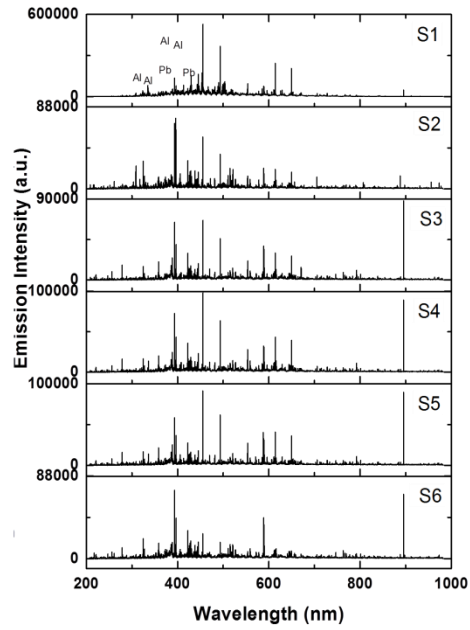
Figure 2. Crater and superficial morphology of waste PCB sample (S2) obtained by scanning electron microscopy (SEM).



← MMC



↙ TP CT

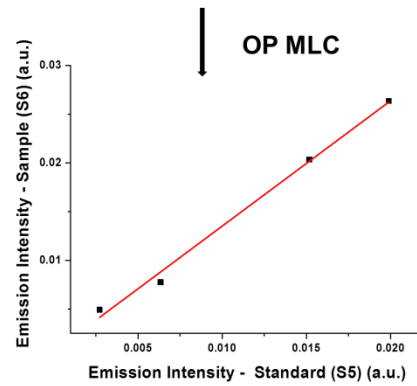


→ CF

$$\ln \frac{I_\lambda}{A_{ki} g_k} = \ln \frac{C_{\text{analyte}}}{U(T)} - \frac{1}{K_B T} E_k$$

↘ SSC

$$C_{\text{analyte}} = \frac{\frac{C_{\text{Al standard}} \times I_{\text{Al sample}}}{I_{\text{Al standard}}}}{\left(\frac{C_{\text{Pb standard}} \times I_{\text{Pb sample}}}{I_{\text{Pb standard}}} \right) + \left(\frac{C_{\text{Mg standard}} \times I_{\text{Mg sample}}}{I_{\text{Mg standard}}} \right)}$$



↓ OP MLC

Figure 1

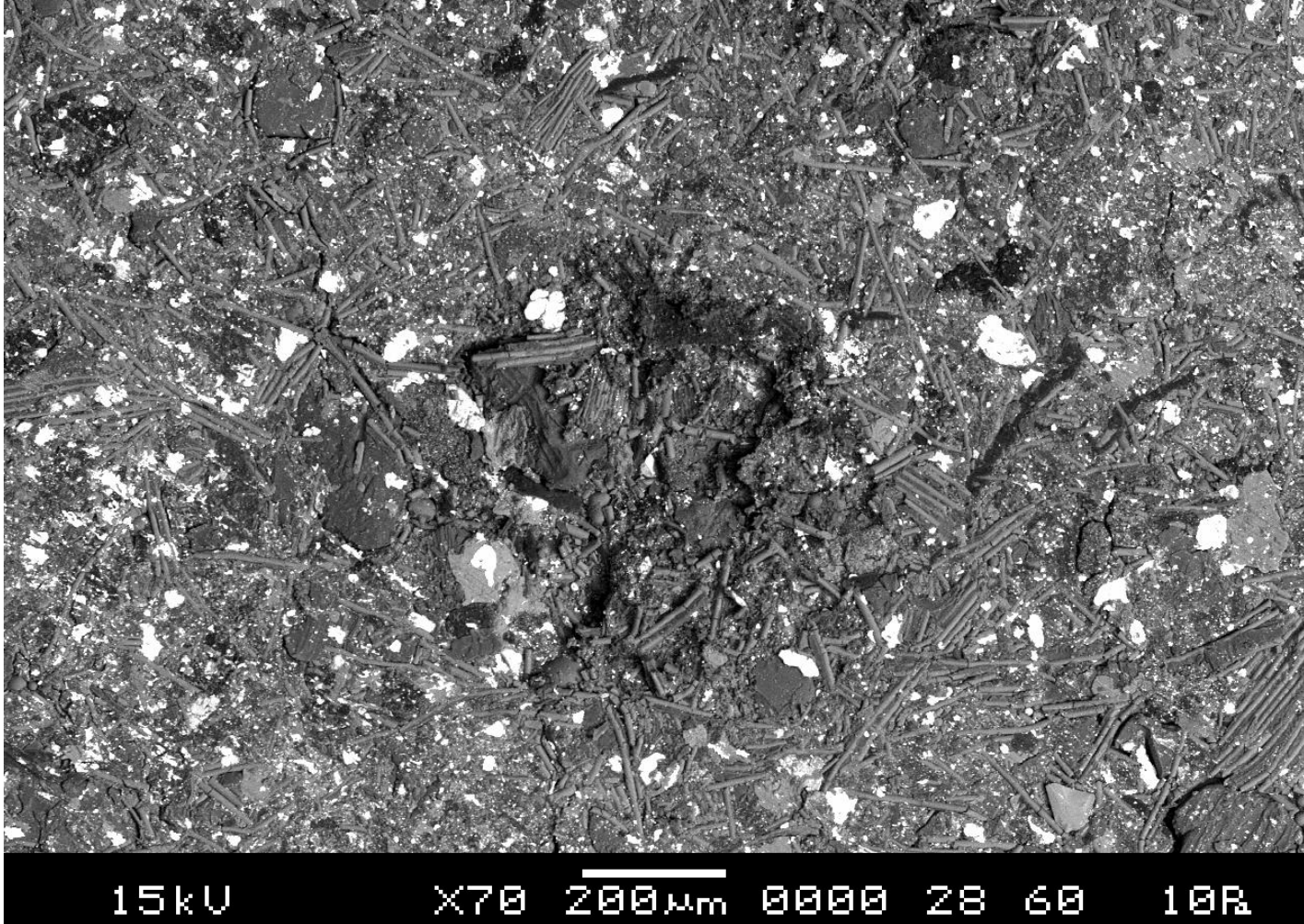


Figure 2

Electronic Supplementary Information (ESI):

Direct determination of Al and Pb in waste printed circuit boards (PCB) by Laser-induced breakdown spectroscopy (LIBS): evaluation of calibration strategies and economic - environmental questions

Diego Victor Babos,^{1,2} Andrés Cruz-Conesa,¹ Edenir Rodrigues Pereira-Filho²
and Jesús Manuel Anzano^{1*}

¹Laser Laboratory, Chemistry & Environment Group, Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

²Group of Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, São Carlos, São Paulo State, 13565-905, Brazil

*Corresponding author:

Jesús Manuel Anzano

Laser Laboratory, Chemistry & Environment Group, Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

Phone number: +34 9 7676 2684

E-mail: janzano@unizar.es (J. Anzano).

This ESI contains:

- 2 Tables
- 2 Figures

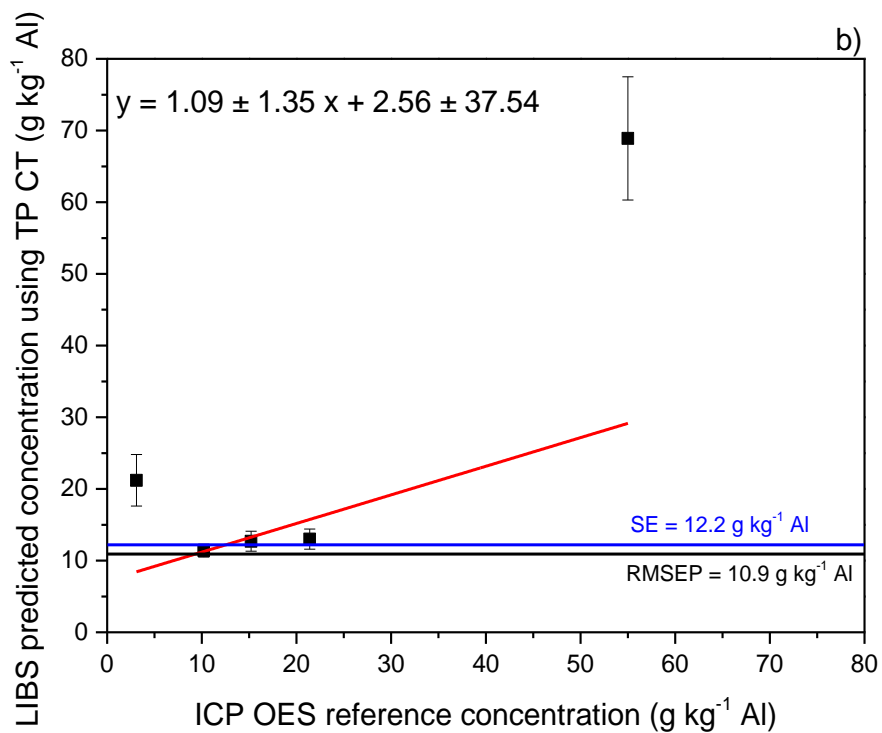
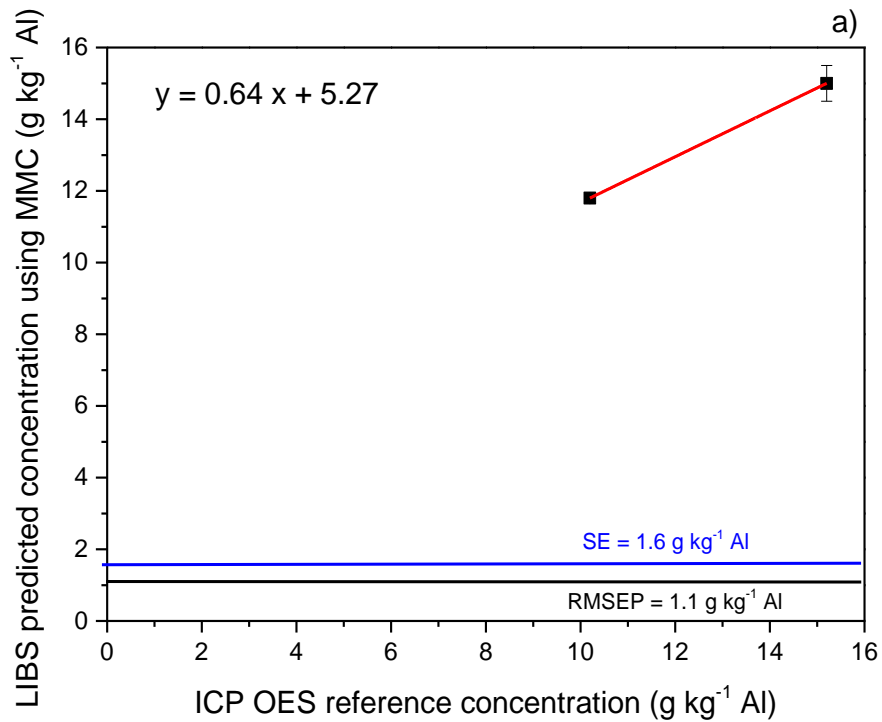
Table S1. Matrix of experiments showing the variables evaluated for optimizing delay time, gate width and laser pulse energy in LIBS determinations. The overall desirability (OD) was used as experimental response.

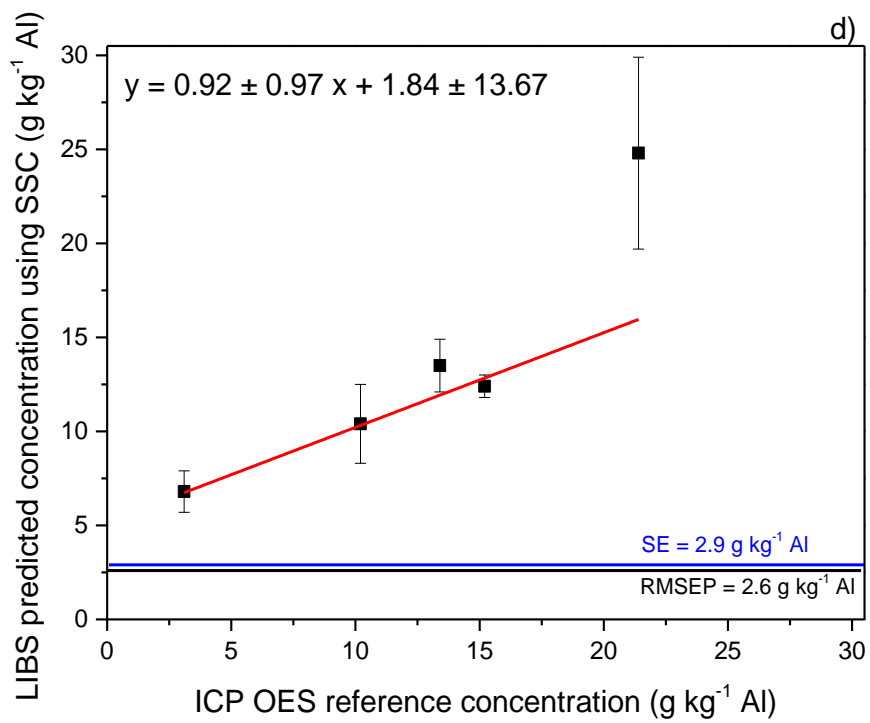
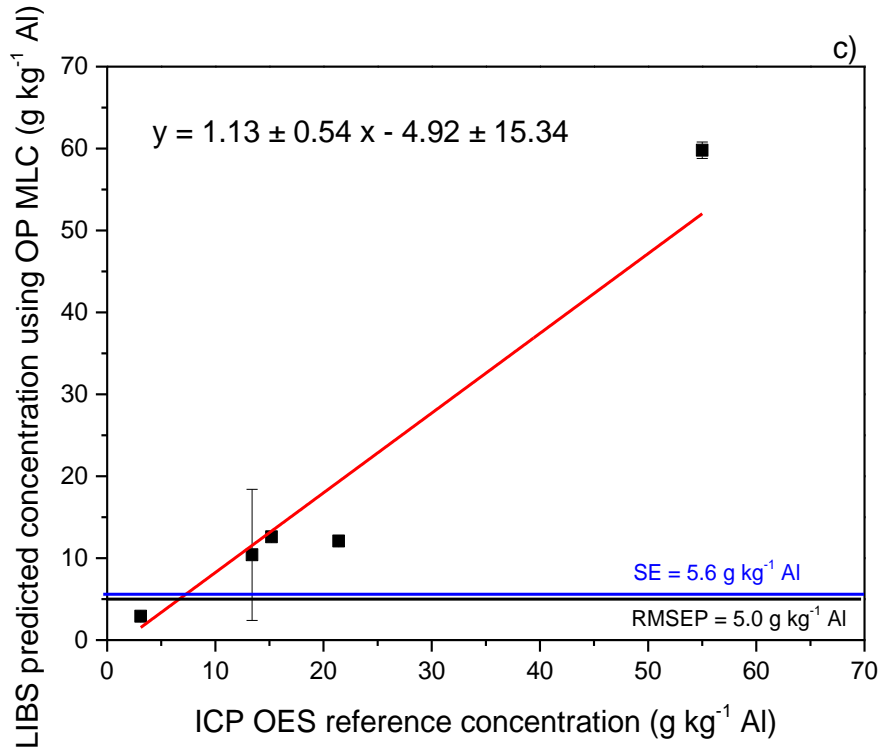
Experiment	Delay time (μs)		Gate width (μs)		Laser pulse energy (mJ)		OD	
	Real	Coded	Real	Coded	Real	Coded		
Full factorial design 2^3	1	0.4	-1	1.0	-1	25	-1	0.49
	2	2.0	1	1.0	-1	25	-1	0.73
	3	0.4	-1	3.0	1	25	-1	0.67
	4	2.0	1	3.0	1	25	-1	0.55
	5	0.4	-1	1.0	-1	42.5	1	0.57
	6	2.0	1	1.0	-1	42.5	1	0.62
	7	0.4	-1	3.0	1	42.5	1	0.30
	8	2.0	1	3.0	1	42.5	1	0.89
Central point	9	1.2	0	2.0	0	35	0	0.44
	10	1.2	0	2.0	0	35	0	0.56
	11	1.2	0	2.0	0	35	0	0.77
	12	1.2	0	2.0	0	35	0	0.61
	13	1.2	0	2.0	0	35	0	0.62
Axial point	14	0.01	-1.49	2.0	0	35	0	0.41
	15	2.54	1.68	2.0	0	35	0	0.74
	16	1.2	0	0.32	-1.68	35	0	0.63
	17	1.2	0	3.68	1.68	35	0	0.64
	18	1.2	0	2.0	0	20	-1.68	0.69
	19	1.2	0	2.0	0	47.5	1.68	0.69

Table S2. Spectroscopic parameters λ (wavelength), E_i (energy of the lower level of transition), E_k (energy of the upper level of transition), A_{ki} (transition probability), and g_k (degeneracy factor of state k) of atomic (I) and ionic (II) lines used in the CF-LIBS calculation. Source: NIST DataBase.

Elements	Line	λ (nm)	E_i (eV)	E_k (eV)	g_k	$A_{ki} \cdot 10^8$ (s ⁻¹)
Al	I	309.271	0.01	4.02	6	0.730
Al	I	783.531	4.02	5.60	6	0.057
Al	I	783.613	4.02	5.60	6	0.004
Ba	II	614.172	0.70	2.72	4	0.412
Ba	II	649.690	0.60	2.51	2	0.130
Ba	I	705.994	1.19	2.95	9	0.500
C	I	247.856	2.68	7.68	3	0.180
Ca	II	317.933	3.03	7.05	6	3.600
Ca	I	558.876	40.05	43.51	7	0.409
Ca	I	612.222	1.89	3.91	3	0.287
Ca	I	616.217	1.90	3.91	3	0.477
Co	I	356.938	0.92	4.40	8	1.500
Cr	II	283.563	1.55	5.92	12	2.000
Cr	I	360.533	0.00	3.44	5	1.620
Cu	I	510.554	1.39	3.82	4	0.020
Cu	I	521.820	3.82	6.19	6	1.220
Cu	I	578.213	1.64	3.79	2	0.019
Fe	II	239.924	0.08	5.25	6	1.400
Fe	I	373.532	0.86	4.18	7	0.270
Fe	I	382.042	0.86	4.10	9	0.668
Fe	I	404.581	1.48	4.55	9	0.863
Fe	I	438.354	1.48	4.31	11	0.500
Mg	I	518.361	2.72	5.11	3	0.561
Mn	II	293.306	1.17	5.40	3	2.040
Ni	I	341.476	0.03	3.66	9	0.550
Ni	I	351.505	0.11	3.64	7	0.420
Ni	I	352.454	0.03	3.54	5	1.000
Pb	I	405.780	1.32	4.38	3	0.912
Sb	I	259.805	1.06	5.83	2	0.210
Si	I	288.158	0.78	5.08	3	1.890
Sn	I	317.050	0.42	4.33	3	0.838
Ti	II	334.941	0.05	3.75	12	1.680
Ti	I	498.173	0.85	3.34	13	0.660
Ti	I	499.107	0.84	3.34	11	0.584
Zn	I	481.053	4.08	6.65	3	0.700

Figure S1. Comparison of Al concentrations determined in waste PCBs samples by the proposed LIBS method using different calibration strategies (a- MMC, b- TP CT, c- OP MLC, d- SSC and e- CF) and the ICP OES reference method. The SE and RMSEP were added as lines parallel to the X-axis.





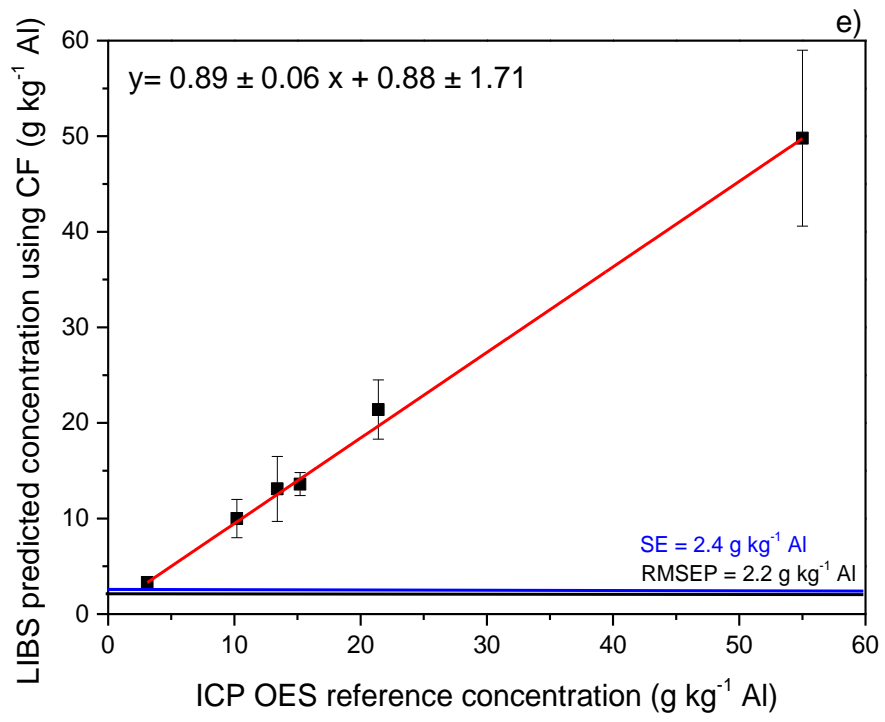


Figure S2. Comparison of Pb concentrations determined in waste PCBs samples by the proposed LIBS method using different calibration strategies (a- MMC, b- TP CT, c- OP MLC, d- SSC and e- CF) and the ICP OES reference method. The SE and RMSEP were added as lines parallel to the X-axis.

