Handheld LIBS Instrumentation Applied to the Rapid Discrimination between Iron Meteorites and Meteor-Wrongs

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Meteorites are rocks that once were part of planets or large asteroids, and usually contain a great amount of extra-terrestrial iron. Nowadays, the meteorite business is booming and the demand is increasing all over the world, whereas supply (originating especially from Morocco and Algeria) is limited. Thus, specimens presented as meteorites often turn out to be common Earth rocks or old smelter and castoff iron dubbed as a “meteor-wrong”. In the present study a compact handheld instrument based on fast-response multi-elemental analysis technique, i.e., laser induced breakdown spectroscopy (LIBS), has been used to identify specific major elements (Ni and Co) and trace elements (Ga and Ir), in order to discriminate a certified iron meteorite with respect to a suspected meteorite fragment and a pig iron product. Furthermore, a calibration free LIBS method has been used to quantify the main elements Fe, Ni and Co in the iron meteorite and Fe, Mn, Si and Ti in the other two fragments.

Keywords: handheld LIBS, iron meteorite, iron meteor-wrong, pig iron, CF-LIBS.
fusion crusts, specific orientations, contraction cracks and rollover lips, which are unique to meteorites (Benedix et al. 2014).

These extra-terrestrial objects, especially iron meteorites, may, however, be confused, either faithfully or by purpose, with terrestrial rocks or manmade iron objects that simulate some typical features of true meteorites. After a careful analysis, a specimen, which is thought or suspected to be an iron meteorite, may show up to be a “pseudometeorite”, or affectionately and humorously named “meteor-wrong”. These materials are attracted by a magnet, and include terrestrial iron oxides such as magnetite, dark black rocks such as basalt, and many different types of man-made iron by-products such as slags from old smelters and castoff iron that have corroded over time. In particular, slags often feature very rough, burned and melted glassy (vitreous) surfaces, and the presence of vesicles (gas bubbles) created by escaping gases. Many slags show flow features in the glass, and some have flat surfaces when solidified in a restricted space.

Genuine meteorites tend to look different from ordinary terrestrial rocks lying around them, but their preliminary identification in the field needs a practiced eye. In particular, meteorites do not contain the common earth mineral quartz, and generally do not present vesicles, whereas when gas escapes from a cooling molten material, it creates small pinprick holes and cavities on the surface. Thus, if a suspected meteorite looks like a sponge, with lots of tiny holes, it is probably a terrestrial volcanic rock or a slag, so an experienced eye will immediately identify this as a meteor-wrong (Notkin 2011). Most meteorites, especially iron meteorites, feel much heavier in the hand than an ordinary earth rock should, and contain a significant amount of extra-terrestrial Fe and Ni, thus the first step in identifying them is the
magnet test, i.e., they stick to a magnet. Many Earth rocks are also attracted by a magnet, so this is not a definitive test, but represents a preliminary proof to further analysis.

Visual and magnetic methods are thus not exhaustive for an unequivocal identification, that requires an adequate laboratory analysis in order to ascertain the extra-terrestrial origin of suspected, especially iron, meteorites (Notkin 2011). In particular, Ni is a rare element on the earth but most often present in meteorites. Hence, if visual inspection and the magnet test are positive, the presence and content of Ni should be verified, together with that of some diagnostic trace elements such as Ga, Ge and Ir. With respect to the various destructive and expensive traditional analytical techniques generally used, the elemental determination performed by laser induced breakdown spectroscopy (LIBS) shows significant advantages, including sensitivity to light elements, versatility, minimal destructivity, rapidity, relatively low operating costs, and the possibility of in-field operations (Cremers and Radziemski 2006, Harmon et al. 2013, Senesi 2014). In previous studies, bench-top (Thompson et al. 2006, De Giacomo et al. 2007, Dell’Aglio et al. 2010, Cousin et al. 2012, Hornackova et al. 2014) and portable (Senesi et al. 2016) LIBS systems showed promise in meteorite analysis. Very recently a portable handheld LIBS instrument, associated with a multivariate calibration treatment of the LIBS spectra acquired in the ultraviolet (UV) and infrared (IR) spectral ranges, was used successfully for the in situ quantitative measurement of Si, Al, Mg, Ca, Ba, Na and Fe mass fractions in weathered terrestrial meteorite analogues (black steel slag and impact glasses) (Gómez-Nubla et al. 2018). In particular, the LIBS predicted concentrations were in good agreement with the certified concentrations measured by XRF. However, a simple and more compact handheld LIBS instrument has not yet been demonstrated for the identification of true meteorites and their discrimination from meteor-wrongs.
In this study, a handheld LIBS instrument was used for the first time to measure the qualitative differences in the elemental composition among a classified and certified iron meteorite named Agoudal, a suspected meteorite fragment and a pig iron product. Further, the quantification of the major elements Fe, Ni and Co in the iron meteorite and Fe, Mn, Si and Ti in the other two samples was attempted using a calibration free (CF)-LIBS method. The performance of LIBS for the rapid discrimination between meteorites and so-called meteor-wrongs has been evaluated.

Materials and methods

Samples

The samples of this study were a certified meteorite, a suspected meteorite fragment and a pig iron produced from the iron industry. The certified meteorite sample was a 51-mm-long fragment of the Agoudal meteorite (Figure 1a), which was discovered and collected from the nearby village in the High Atlas Mountains in Morocco (Chennaoui Aoudjehane et al. 2013, Meteoritical Bulletin Database 2014). This meteorite consists of abundant coarse-grained kamacite (α-Fe, Ni), with a ratio Fe:Ni between 90:10 and 95:5, schreibersite (Fe,Ni)₃P, rhabdite (tetragonal schreibersite) and troilite (FeS) (Chennaoui Aoudjehane et al. 2013, Schmieder et al. 2015). The quantitative ICP-MS analysis ascertained a content of 5.5% m/m Ni and 4.1 mg g⁻¹ Co, and trace levels of Ga (58 μg g⁻¹), Ir (< 0.04 μg g⁻¹) and Au (~ 1 μg g⁻¹), thus this meteorite is assigned to the IIAB magmatic iron group (Chennaoui Aoudjehane et al. 2013).
The suspected meteorite (Figure 2) was collected in a dry valley in the High Atlas Mountains in Morocco, which was located half way from the villages of Imilchil and Agoudal, close to the site where the Agoudal iron meteorite was discovered. Based only on visual inspection and field tests the fragment (Figure 1b) was identified as an iron meteorite, but its composition was totally unknown, thus only a detailed chemical analysis in the laboratory might guarantee its genuineness. The pig iron sample (Figure 1c) was an intermediate product of the iron industry originated from an industrial source, and consisted of a very brittle iron-carbon-silicon alloy obtained by smelting in a blast furnace an iron ore as the basic ingredient before further processing to produce the desired grades of steel.

Handheld LIBS

A portable, compact handheld LIBS instrument named NanoLIBS (B&W Tek, Newark, DE, USA) was used to analyse the samples. The instrument consists of a miniature-diode-pumped, solid-state, short-pulsed laser emitting at the wavelength of 1064 nm with a maximum output of 300 mW, a pulse duration of 500 ps and a maximum pulse energy of 150 µJ, and operating at a high repetition rate, i.e. between 1 and 5 kHz. Measurements were performed by placing the instrument against the sample surface and then the analysis was started via a trigger.

The spectra were recorded by a compact spectrometer operating in the non-gated mode with an overall resolution of 0.4 nm over the entire wavelength acquisition range from 180 to 800 nm, i.e. from UV to visible. The integration time of the spectrometer was set at 4 ms, which
corresponds to twelve laser pulses for a 1-kHz laser. The spectrometer and the acquisition settings were controlled by a liquid crystal display (LCD) touch screen panel.

The system is equipped with a rastering beam that covered an area with a diameter of about 300 μm. As the samples were not homogeneous, ten different positions were analysed and each measurement lasted about 6 s. On each position a total of 150 spectra corresponding to 1800 laser shots were acquired and averaged to obtain a single spectrum. The average LIBS spectra were stored in the analyser and accessed using a Linux operating system with graphic user interface (GUI) by downloading via Wi-Fi or Ethernet. Then, the spectra were analysed qualitatively using the NIST database, and quantitatively by applying the CF-LIBS method implemented by proprietary software (LIBS++ by Marwan Technologies).

For safety reasons, the laser output was controlled automatically by a sensor installed in the analytical head, so that the laser could operate only when the analytical head was in contact with the sample. The NanoLIBS instrument is designed to operate primarily as a handheld device outdoor in the field, thus it is provided with a rechargeable Li-ion battery allowing up to 8 h of operation. However, it can also operate indoor while connected to AC power. The whole system is enveloped in a lightweight and compact (mass and dimensions of approximately 1.8 kg and 26 cm × 10 cm × 30 cm, respectively), handheld body.

**Scanning electron microscopy and X-ray fluorescence spectrometry**

The reference quantitative analysis of the suspected meteorite sample was conducted by scanning electron microscopy (SEM) coupled with microanalysis. The instrument used is a field emission SEM (Zeiss SIGMA 300 VP) operated in both high vacuum and variable
pressure modes with a resolution of ~ 10 nm, and was equipped with backscattered electron
(BSE) detectors, an in-lens secondary electron (SE) detector and a cathodoluminescence (CL)
detector. The elemental composition was measured by two energy dispersive X-ray
spectroscopy (EDS) systems equipped with silicon drift detectors (SDD) of 60 and 44 mm²
having a resolution of 123 eV (Bruker).

The pig iron sample was analysed preliminarily by X-ray fluorescence (XRF) spectrometry
using a MagiX FAST simultaneous XRF instrument (PANalytical B.V., Holland) equipped
with a 300-µm brass filter, a 1-mm Pb beam-stop and a 4 kW Rh Super Sharp end-window
Tube set at 60 kV and 66 mA to obtain the optimal measurement of heavier elements.

Results and discussion

Qualitative LIBS analysis

The analysis of the broad emission spectra measured on the three samples showed that the
main components of the Agoudal meteorite were Fe, Ni and Co, whereas those of the other
two samples were Fe, Mn, Si and Ti. All the spectra featured an intense background
especially in the wavelength range of 200–300 nm where multiple lines of the major matrix
element, Fe, appeared.

The laser energy used in the handheld LIBS instrument was lower than that used in
conventional LIBS, so producing a smaller-sized, lower intensity plasma yielding a lower,
short time continuum radiation. However, the spectrometer was used in the non-gated mode
and about twelve ablations occurred during one gate time, thus the appearance of a
background signal was unavoidable. Similar effects were observed by other authors (Afgan et al. 2017) in analysing steel samples by a handheld LIBS system.

Due to the dominant presence of Fe lines in the spectra of the three samples, the main differences among them could be revealed only when examining the specific spectral ranges from 215 to 240 nm (Figure 3a) and from 330 to 355 nm (Figure 3b). In particular, in the spectral range 215–240 nm, besides several emission lines of the major elements Co II and Ni II, the specific signals of the typical trace metals Ga I (at 225.503 and 229.787 nm) and Ir I and Ir II (at 220.809, 226.633 and 230.422 nm) were evident in the iron meteorite spectrum, but not in that of the other two samples.

Differently, in the more crowded range 330–355 nm the typical spectral lines of Ti I (at 332.294, 332.946, 334.941 and 336.121 nm) and Si II (at 333.982 nm) were present in the pig iron sample, but not in the iron meteorite and in the other fragment. Further, the spectrum of the iron meteorite in this range featured some specific spectral lines of Ni I at 336.957, 338.057, 339.105, 341.348, 342.371, 345.857, 349.296 and 352.454 nm, Co I at 340.512, 343.158, 344.364 and 347.402 nm and Ir I at 351.364, which were not present in the other two samples. Thus, the handheld LIBS instrument was able to identify and discriminate the qualitative chemical elemental composition of the three samples examined by showing a number of relevant differences among them. In particular, the absence of Ga and Ir in the suspected meteorite fragment, which was erroneously classified by all field tests as a true iron meteorite, indicated that this fragment is actually a meteor-wrong, probably an old, rusted cast iron residue.
The NIST DataBase values (NIST ASD Team 2018) of the spectroscopic parameters of the most intense spectral lines of the major elements identified in the samples are listed in Table 1. Only the most intense lines, which were not overlapped by signals of other elements, were selected for the further quantification process. In particular, in the pig iron sample the C signal at 247.856 nm was overlapped by Fe signals because of the high concentration of Fe and the low resolution of the miniaturised spectrometer, whereas the spectral lines of Co, Ni, Ga and Ir could be identified in the Agoudal meteorite sample because of reduced Fe line interferences. Furthermore, self-absorbing lines featuring high values of $g_k \cdot A_{ki}$ were identified and discarded from quantification, because self-absorption weakens their intensity, thus the concentration of the corresponding elements could be underestimated with an impact more marked on major elements than on trace elements.

< Table 1 here>

**Quantitative CF-LIBS analysis**

On the basis of the most intense, reproducible and sensible spectral lines, the major elements chosen to be quantified by CF-LIBS analysis were, respectively, Fe, Ni and Co for the iron meteorite, and Fe, Mn, Si and Ti for the other two samples. The LIBS measurement of the C content in iron materials is still a challenging task even when using conventional bench-top LIBS systems, because most of the C lines appear in the VUV range, i.e. they are absorbed in air. Further, the strongest detectable C line at 247.856 nm is located in the range of the crowded Fe spectrum.
In the case of iron meteorites, a particularly important issue concerns the determination of their quantitative elemental composition as they are classified on the basis of either their Ni content or on the different phases in which they crystallise. Iron meteorites can be further assigned to various subclasses on the basis of trace element (mainly Ga, Ge, Ir) contents that are influenced markedly by the cooling history of the meteorite, and can therefore provide important information on their parent bodies (Goldstein and Scott 2009). Although the emissions peaks of some of these trace elements (Table 1) have been detected, no quantification has been attempted before now because of the large uncertainties of the CF-LIBS method when determining elemental mass fractions lower than hundreds of µg g⁻¹ (Dell’Aglio et al. 2010).

The CF-LIBS procedure implies the assumption of the existence of the Local Thermodynamic Equilibrium (LTE) in the plasma, and its correct application requires the accurate determination of several parameters of the laser induced plasma, including its temperature and electron density, which can be measured by the intensities and profiles of spectral emission lines (Ciucci et al. 1999, Cremers and Radziemski 2006). In this work, the excitation temperature \( T_{\text{ex}} \) values obtained by the Fe Boltzmann plot of all spots analysed was about 12000 K for all samples, whereas the electron density \( N_e \) values obtained by the Stark broadening of the hydrogen line were \( 5.63 \times 10^{17} \text{ cm}^{-3} \) for the Agoudal meteorite and \( 5.29 \times 10^{17} \text{ cm}^{-3} \) and \( 7.69 \times 10^{17} \text{ cm}^{-3} \), respectively, for the suspected meteorite and the pig iron samples. These results confirmed that the LTE condition was fulfilled \( (T_{\text{ex}} > 5000 \text{ K, } N_e > 1016 \text{ cm}^{-3}) \) in the plasma generated by each sample examined. Further, the plasma conditions of all samples were comparable as the experimental uncertainty of \( T_{\text{ex}} \) and \( N_e \) values were of 10–15%. Some slightly higher deviations might be due to small differences in the ablation efficiency and/or to the different dimensions of the sample grains and/or minerals.
The quantitative composition of the Agoudal meteorite obtained by the CF treatment of data measured by the handheld LIBS instrument showed some differences from the corresponding data obtained in a previous study by a portable µ-LIBS system (Senesi et al. 2016) and the reference ICP-MS data from the literature (Chennaoui Aoudjehane et al. 2013) (Table 2). Although the Fe content was in good agreement, differences were found for Ni and Co contents measured by the three techniques. The differences between the two LIBS systems might probably be due to the double-pulse LIBS setting used in the portable system, which improved its sensitivity, and to the low resolution of the spectrometers used in the handheld system as a consequence of the intense spectral background. Further, the differences observed between LIBS and ICP-MS data might be ascribed to the much greater amount of sample (about 1 g) that can be analysed by ICP-MS, which reduces markedly the matrix effects, with respect to the amount analysed by LIBS, which is a point analysis technique able to consider only a very small portion of the sample corresponding to the dimension of the focused laser spot. However, an improvement of the analytical performance of LIBS, so to approach, from the statistical point of view, the values obtained by other techniques, could be achieved by moving the sample during LIBS analysis in order to ablate different points.

The quantitative composition of the pig iron and the already ascertained meteor-wrong samples measured by the two CF-LIBS systems, EDS-SEM and XRF are shown in Table 3. Also for these samples a good agreement was shown between the two techniques for the Fe content. In the case of the pig iron sample, also the Ti and Si contents measured by XRF were quite similar to those obtained by the handheld LIBS instrument, whereas the content of Mn appeared overestimated by LIBS.
No detectable amounts of Ni and Co were found in the meteor-wrong sample by either EDS-SEM or LIBS (LOD = 0.009% for Ni and 0.003% for Co), which was confirmed by BSE imaging and EDS X-ray mapping. The BSE image (Figure 4, left) showed the presence of spheroidal graphite (grey zone) and microstructures consistent with iron materials containing P (black zone). The EDS X-ray elemental maps (Figure 4, right) indicated a marked presence of Fe and P and a minor presence of C, whereas Mn was not detectable. Although P and S, which are generally present as sulfide and phosphide accessory minerals, could be detected by LIBS in the deep UV range, between 175 and 190 nm, this would require the use of an argon purge that was not available in the handheld instrumental configuration used in this work. Thus, even if the quantitative data obtained by traditional techniques are not always in good agreement with LIBS data, the quantitative results obtained appear enough to suggest that the suspected meteorite fragment was a meteor-wrong, and very probably consisted of an ancient fragment of cast iron.

Conclusions

The results of the direct LIBS analysis of the documented Agoudal iron meteorite, a suspected meteorite fragment and a pig iron sample demonstrated the good performance of the handheld LIBS instrument when used for the rapid and trustable authentication of iron meteorites. In particular, the qualitative analysis made by the handheld LIBS system, even if
equipped with a low resolution spectrometer, allowed the identification of the major elements Fe, Ni and Co and the trace elements Ga and Ir only in the iron meteorite, which confirmed the high potentiality of this technique in discriminating a true iron meteorite sample from a meteor-wrong sample. However, the LIBS quantitative data were only partly satisfactory, and require adequate improvements of some LIBS instrumental parts to increase the analytical sensitivity.

In conclusion, the handheld LIBS instrument appears to represent a promising advanced technical tool to obtain a fast, reliable, non-destructive, in-field chemical analysis and identification of the extra-terrestrial origin of metallic objects with respect to human artefacts, so being able to discriminate between a true meteorite and a meteor-wrong. Furthermore, the preliminary chemical classification of iron meteorites could be used in the near future to identify and recognise mislabelled/unlabelled dubious meteorite specimens in museums and private collections.

Acknowledgements

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Laser-induced breakdown spectroscopy (LIBS) applied to terrestrial and extra-terrestrial
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Figure 1. Fragments of the Agoudal meteorite (a) the suspected meteorite (b), and the pig iron sample (c).

Figure 2. The suspected meteorite (shown at left above) and its location (shown by the red marker on the map at upper right).

Figure 3. LIBS spectra in the ranges from 215 to 240 nm (a) and from 330 to 355 nm (b) of the Agoudal iron meteorite, the suspected meteorite and the pig iron sample.

Figure 4. BSE image (left) and EDS X-ray elemental maps of C, Fe, P in a selected area of the meteor-wrong fragment.

Figure captions

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Figure 4. BSE image (left) and EDS X-ray elemental maps of C, Fe, P in a selected area of the meteor-wrong fragment.
Table 1.
Spectroscopic data* of the main atomic emission lines identified in the samples examined (source: NIST ASD Team 2018)

<table>
<thead>
<tr>
<th>Element</th>
<th>λ_{lk} (nm)</th>
<th>E_{l}-E_{k} (eV)</th>
<th>A_{nl} (10^{8} s^{-1})</th>
<th>g_{r}-g_{k}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co I</td>
<td>340.512</td>
<td>0.432–4.072</td>
<td>1E +0</td>
<td>10–10</td>
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<td></td>
<td>343.158</td>
<td>0.101–3.713</td>
<td>6.6E -1</td>
<td>8–6</td>
</tr>
<tr>
<td></td>
<td>344.364</td>
<td>0.514–4.113</td>
<td>5.5E +0</td>
<td>8–8</td>
</tr>
<tr>
<td></td>
<td>347.402</td>
<td>0.582–4.149</td>
<td>4.5E +0</td>
<td>6–8</td>
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<tr>
<td>Fe II</td>
<td>238.203</td>
<td>0.0–5.203</td>
<td>3.8E +01</td>
<td>10–12</td>
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<tr>
<td></td>
<td>258.587</td>
<td>0.0–4.793</td>
<td>7.15E +0</td>
<td>10–8</td>
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<td></td>
<td>259.939</td>
<td>0.0–4.768</td>
<td>2.35E +01</td>
<td>10–10</td>
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<tr>
<td>Fe I</td>
<td>293.690</td>
<td>0.0–4.220</td>
<td>1.26E +0</td>
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<tr>
<td></td>
<td>302.064</td>
<td>0.0–4.103</td>
<td>6.83E +0</td>
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<td>404.581</td>
<td>1.484–4.549</td>
<td>7.76E +0</td>
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<tr>
<td></td>
<td>438.354</td>
<td>1.485–4.312</td>
<td>5.50E +0</td>
<td>9–11</td>
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<tr>
<td>Ga I</td>
<td>225.503</td>
<td>0.0–5.497</td>
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<tr>
<td></td>
<td>229.787</td>
<td>0.102–5.497</td>
<td>1.11E -1</td>
<td>4–2</td>
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<tr>
<td>Ir I</td>
<td>220.809</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>226.633</td>
<td>0.784–6.253</td>
<td>1.53E -1</td>
<td>8–10</td>
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<tr>
<td></td>
<td>230.422</td>
<td>0.351–5.731</td>
<td>3.28E -1</td>
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<td>351.364</td>
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<td>Mn II</td>
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<td>8E +0</td>
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<td>294.921</td>
<td>1.175–5.377</td>
<td>1.37E +01</td>
<td>5–7</td>
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<td>Ni I</td>
<td>336.957</td>
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<td>5.9E -1</td>
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<td></td>
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<td>0.165–3.796</td>
<td>1.9E -1</td>
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<td>342.371</td>
<td>0.212–3.833</td>
<td>9.9E -1</td>
<td>3–3</td>
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<tr>
<td></td>
<td>345.857</td>
<td>0.212–3.796</td>
<td>3.0E +0</td>
<td>3–5</td>
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<table>
<thead>
<tr>
<th>Element</th>
<th>ICP-MS*</th>
<th>CF-LIBS**</th>
<th>CF-LIBS***</th>
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<tr>
<td>Fe</td>
<td>94.1</td>
<td>94.94 ± 0.43</td>
<td>96.85</td>
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<tr>
<td>Ni</td>
<td>5.5</td>
<td>4.72 ± 0.43</td>
<td>2.55</td>
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<tr>
<td>Co</td>
<td>0.41</td>
<td>0.58 ± 0.3</td>
<td>0.60</td>
</tr>
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</table>

*Reference ICP-MS data from the literature (Chennaoui Aoudjehane et al. 2013).

**Portable µ-LIBS data (Senesi et al. 2016).

***Handheld LIBS data of this work.
Table 3.

Mass fractions (in % m/m) of Fe, C, Si, Mn, Ti and P in the meteor-wrong and pig iron samples measured in this work by different techniques.

<table>
<thead>
<tr>
<th>Element</th>
<th>EDS-SEM</th>
<th>CF-LIBS</th>
<th>XRF</th>
<th>CF-LIBS</th>
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<td></td>
<td>Meteor-wrong</td>
<td>Meteor-wrong</td>
<td>Pig iron</td>
<td>Pig iron</td>
</tr>
<tr>
<td>Fe</td>
<td>96.67 ± 1.56</td>
<td>97.18</td>
<td>92.4</td>
<td>95.93</td>
</tr>
<tr>
<td>C</td>
<td>1.33 ± 1.08</td>
<td>&lt; 0.008*</td>
<td>4.92</td>
<td>&lt; 0.008*</td>
</tr>
<tr>
<td>Si</td>
<td>0.68 ± 0.08</td>
<td>1.91</td>
<td>2.08</td>
<td>1.43</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt; 0.24**</td>
<td>0.91</td>
<td>0.158</td>
<td>2.51</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt; 0.18**</td>
<td>&lt; 0.0009*</td>
<td>0.118</td>
<td>0.12</td>
</tr>
<tr>
<td>P</td>
<td>1.32 ± 0.57</td>
<td>&lt; 0.0013*</td>
<td>0.104</td>
<td>&lt; 0.0013*</td>
</tr>
</tbody>
</table>

*Limit of detection by LIBS
**Limit of detection by EDS-SEM