Comparison of Elemental Analysis Techniques for the Characterization of Commercial Alloys

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Abstract: Better quality control for alloy manufacturing and sorting of post-consumer scraps relies heavily on the accurate determination of their chemical composition. In recent decades, analytical techniques, such as X-ray fluorescence spectroscopy (XRF), laser-induced breakdown spectroscopy (LIBS), and spark optical emission spectroscopy (spark-OES), found widespread use in the metal industry, though only a few studies were published about the comparison of these techniques for commercially available alloys. Hence, we conducted a study on the evaluation of four analytical techniques (energy-dispersive XRF, wavelength-dispersive XRF, LIBS, and spark-OES) for the determination of metal sample composition. It focuses on the quantitative analysis of nine commercial alloys, representing the three most important alloy classes: copper, aluminum, and steel. First, spark-OES is proven to serve as a validation technique in the use of certified alloy reference samples. Following an examination of the lateral homogeneity by XRF, the results of the techniques are compared, and reasons for deviations are discussed. Finally, a more general evaluation of each technique with its capabilities and limitations is given, taking operation-relevant parameters, such as measurement speed and calibration effort, into account. This study shall serve as a guide for the routine use of these methods in metal producing and recycling industries.

Keywords: alloy analysis; impurities; spectroscopy; quality control

1. Introduction

Metal alloys are a highly important class of compounds, which are found in everyone's daily life. Because of their widespread use in manifold applications, their production possesses a high economic importance and acts as an indicator for the overall state of the global economy. In many cases, recycling of alloys for the production of new ones is more energy-efficient and environmental-friendly, reducing the high CO2 footprint linked to metal production [1,2]. One of the main obstacles for cost- and energy-efficient metal recycling is the contamination of post-consumer scraps with several metal impurities. In this case, the re-smelting of the scrap to produce a new target alloy within certain elemental concentration limits is only possible by adding primary raw material in the smelting process [3]. To avoid this so-called downcycling effect, the contaminations in the post-consumer scraps need to be identified and treated separately. The accurate identification of modern, mixed waste fractions, containing impurities of a variety of metals in % to ppm-range, is challenging for most of the state-of-the-art analysis techniques, but essential for closing loops in current metal production chains [4]. Even the characterization of less complex pure
alloys, i.e., not mixed, non-oxidized metal compounds, bears several obstacles to correct identification and quantification of the constituting components. For example, an accurate determination of the chemical composition will help in the process control of the production of complex alloys with additives, such as layered alloy stacks or superalloys [5]. In addition, a better characterization of the alloys can be beneficial for the tuning of their further mechanical or chemical treatment, e.g., in the comminution of such materials by mills [6]. The determination of the chemical constitution of oxidized scrap pieces that consist of several mixed alloys in a real-world recycling process is more complicated.

In the past decades, manifold analytical techniques have been employed to analyze the (micro-)structure and chemical composition of pure metals and alloys [7]. Especially for the identification and quantitative analysis of main and trace elements, different sophisticated methods, such as inductively-coupled plasma optical emission spectroscopy/mass spectrometry (ICP-OES/MS) [8], laser-induced breakdown spectroscopy (LIBS) [9,10] were evaluated. While for ICP-OES/MS the material to be analyzed has to be present in a liquid or gaseous state, for LIBS experiments solid samples can be used as well. Other OES methods commonly employed for metal and alloy analyses are spark spectrometry (spark-OES) and glow-discharge OES, which use high-energetic electrical arcs to form the plasma [11,12]. Besides the OES techniques, X-ray fluorescence spectroscopy (XRF) methods are used as well for the determination of major and minor element concentrations in alloys [13]. They can be divided into two main groups, based on their characteristic principle of dispersive X-ray detection. While energy-dispersive XRF (EDXRF) uses an energy-dispersive silicon drift detector (SDD), wavelength-dispersive XRF (WDXRF) employs diffraction crystals to disperse the recorded radiation at element-specific wavelengths, based on Bragg’s law. EDXRF systems are cheaper, more compact, and more often found in portable handheld devices (pXRF). WDXRF systems are often equipped with detectors that possess a higher spectral resolution but receive less signal per second compared to modern energy-dispersive SDDs. Thus, such systems are often found in dedicated metal analysis laboratories for ex situ experiments.

Despite the existence of such a variety of methods for the compositional analysis of metals and alloys and their routine use in the metal-producing and recycling industry, only a few research studies deal with the comparison of analytical techniques for the investigation of real scrap streams, such as production scraps and post-consumer scraps [14–16]. Up to now, most publications on method comparison focused on well-defined, pure alloys, which do not represent the waste streams that the recycling industry has to deal with in daily routine.

This lack of studies motivated us to compare different analytical techniques that are commonly used in industrial practice and evaluate the results of their alloy chemistry determination. This publication shall serve as a practical guide for users in the field of metal recycling who employ (or planning to employ) such analytical tools routinely and are often not fully aware of their potential and limits. The present study focuses on the investigation of commercially available metal alloys, which can be regarded as representative for production scrap. First, we compare our LIBS, EDXRF, and WDXRF results for the test alloys with unknown chemical composition to a more accurate dataset. Although spark-OES is accepted as widely employed, reliable, and accurate technique for the quantification of metal alloys [11], this has to be proven by performing measurement with our spark-OES systems on samples with certified chemistry. Thus, we will demonstrate by the use of certified reference materials (in our case certified reference alloys-CRA) that spark-OES is a suitable validation method, against which the results from our LIBS, EDXRF, and WDXRF experiments can be benchmarked. Second, the results of statistical tests are presented, which were conducted to determine the spatial homogeneity. Finally, the results from LIBS, EDXRF, and WDXRF experiments with nine different test alloys are compared and discussed. The nine alloys belong to the three main metal matrices being produced by the metal industry: Al alloys, Cu alloys, and steels.
2. Materials and Methods
2.1. Samples

For the validation of the spark-OES with some standards of known composition, nine CRAs were used, comprising three steel samples (ZRM 192-1, ZRM 284-3, ZRM 297-1), three Al alloys (EB 313, BAM-311, EB 315a), and three Cu alloys (BAM-367, BAM-378, BAM-394a) acquired from the Bundesanstalt für Materialprüfung (BAM), Germany. They are solid cylindrical blocks with a diameter of 50 mm and a height of 20 mm. Their surfaces are flat-cut, but not polished to be comparable to the state of the test alloy surfaces.

For the comparison of the analytical techniques, nine commercially available alloys (‘test alloys’) were acquired, which are widely used in industrial applications (Table 1). The test alloys were chosen in order to represent a large variety of chemical compositions, especially ones that are linked to a certain measurement problem. For example, two Al alloys, AlMg4.5Mn and AlSi1MgMn, contain aluminum and other light elements, such as magnesium and silicon, as well. These elemental mixtures are reported to pose difficulties for correct quantification by XRF analyses [17]. Contrary to the CRAs, the exact compositions of the test alloys are not known, only concentration limits are given by the corresponding European standards [18,19]. These limits are listed in the Supplementary Information, in Table S1. Each of the nine test alloy bars was cut into 15 equally sized pieces to obtain compact, cuboid, or cylindrical blocks with a surface length of 80 mm (cuboid) or a diameter of 50 mm (cylinders), respectively (Figure 1). Especially in the case of the low-alloyed carbon steel, 42CrMo4, the long-time exposed surface varies considerably from the freshly cut due to its corrosion behavior. Thus, before any experiment with this material the surface was freshly ground to remove the ferrous oxide layers.

Table 1. Used test alloys with common abbreviations indicating quantities of their main elements. In addition, the industry material numbers, defined by European standards (EN) and their main application in industry are given. Each alloy can be linked to analytical challenges, which need to be addressed by the following investigation.

| Alloy Name | Material Number | Main Applications | Analytical Challenge |
|------------|-----------------|-------------------|---------------------|
| Al99.5     | AW 1050 A       | Machining, plant construction | Low content of minor elements |
| AlMg4.5Mn  | AW 5083         | Shipbuilding, pressure vessels | Mixture of light elements Al and Mg |
| AlSi1MgMn  | AW 6082         | Food industry, packaging | Mixture of light elements Al, Mg, and Si |
| CuNi10Fe1Mn| CW 352H         | Water pipes, capacitors | Mixture of several transition metals |
| CuZn39Pb3  | CW 614N         | Tool manufacturing, electronics | Accurate detection of heavy elements |
| CuSn8      | CW 453K         | Spring, pin connectors | Accurate detection of heavy elements |
| X5CrNi18-10| 1.4301          | Building material, sanitation | Detection of multi-element composition |
| 45NiCrMo   | 1.2767          | Tool manufacturing, plastic forming | Low content of minor elements |
| 42CrMo4    | 1.7225          | Automotive, mechanical engineering | Penetration of rusty surface |

Figure 1. Photos of samples from three different classes of test alloys (left) after cutting and an exemplary piece after the measurements (right). The visible surface is cut and exposed to the different sensors. At the black marked spots pXRF spectra were acquired, the raster area of the LIBS laser is well visible as regular pattern of 10–20 µm deep holes.
2.2. Analysis Methods

Four different analysis methods were employed to determine the composition of the test alloys: EDXRF, WDXRF, LIBS, and spark-OES. The latter should serve as a validation method against which the results from the other three techniques are benchmarked.

2.2.1. Spark-OES

Spark-OES has been used as a technique for benchmarking the results from LIBS, WDXRF, and EDXRF. Our samples can be divided into three distinct main metal matrices (Al, Fe, Cu), thus, three different calibrations had to be used. Unfortunately, no single spark spectrometer with all three calibrations was available. Instead, we employed three different spark-OES, specialized in the analysis of one metal matrix. Prior to all spark-OES experiments, the sample surfaces were ground to create a fresh measurement area. The acquisition time was set to ca. 15 s per individual measurement point.

For the analysis of the Al alloys, a spark-OES device ARL 4460 (Thermo Fisher Scientific, Waltham, MA, USA) was used which is located at the Institute for Nonferrous Metallurgy and Purest Materials at the TU Bergakademie Freiberg, Freiberg, Germany. This apparatus is calibrated for the determination of the composition of Al alloys.

In addition, a Foundry-Master UV spark-OES device (Hitachi High-Tech Analytical Science GmbH, Uedem, Germany) device was used, which is located at the Institute of Iron and Steel Technology at the TU Bergakademie Freiberg. It is specialized in the analysis of steels and was dedicated to the CRAs and test alloys, employing special analysis programs and calibrations for low-alloy and high-alloy steel matrices.

For the determination of the Cu alloy compositions, a spark-OES device Spectro Maxx F CCD (Spectro Analytical Instruments, Kleve, Germany) was used. This instrument is dedicated to the routine analysis of Cu alloys in the laboratory of a large Cu alloy manufacturer.

2.2.2. EDXRF/pXRF

For the EDXRF experiments, we used a portable XRF device (pXRF) that is widely used throughout the metal and recycling industry for the first control of incoming scrap fractions. We employed an S1 Titan 600 model (Bruker, Billerica, MA, USA) with a large area CubeTM silicon drift detector which provides an energy resolution of 140 eV at Mn Kα. In combination with a polymer UltraleneTM window, it is able to detect the elemental range from magnesium to uranium. With its light weight of ca. 1.5 kg and in-built acquisition and analysis software, the pXRF is usable as a stand-alone device and in a radiation-safe closed box as well (Figure 2). The X-ray tube is equipped with an Rh target, allowing for a maximal acceleration voltage of 50 kV. We used acceleration voltages between 15 kV and 50 kV and emission currents between 12 µA and 106 µA, depending on the pre-calibrated program for different alloy classes and concentration ranges. The device has an automatic mode for the selection of individual filter settings (Cu 75 µm/Ti 25 µm/Al 200 µm, Al 38 µm, Ti 25 µm/Al 300 µm, or Fe 25 µm) which are applied after the first seconds of measurement, when the instrument has determined the sample matrix (e.g., high-alloyed stainless steel). The measurement spot is around 4 mm in diameter. Preliminary time-dependent experiments proved that an acquisition time of 60 s, split into 30 s acquisition time frames for the light and heavy elements scan each, is a good balance between time effort and result precision. Similar set-ups are used in routine alloy analysis at scrapyards and metal processing plants. The pXRF Bruker Toolbox software contains an ‘Alloys’ mode which uses a pre-built calibration database for element quantification and material identification of the commonly analyzed alloys.

2.2.3. WDXRF

For the WDXRF analysis of the test alloys, the measurements were performed using an AxiosMAX (PANalytical, Almelo, The Netherlands) wavelength-dispersive X-ray fluorescence spectrometer (Figure 2) and the SuperQ software, version 5.3 from the same company. The device is equipped with an X-ray tube with Rh anode, generating a maximum tube power of 4 kW for the primary beam. The acceleration voltages range between 32 kV and 60 kV.
and the emission currents between 66 mA and 125 mA. The samples were placed into steel cups with a 6 mm aperture and measured in vacuum. Three different procedures were created to analyze the samples from the three different base metal classes (steels, Cu alloys, Al alloys). Measurement times were set to 430 s for steels and 570 s for both Al and Cu alloys, respectively. The three applications are set up with three detectors (scintillation detector, gas flow detector, sealed gas detector), without tube filters, three crystals (LiF220, PE 002-C, PX1) and three collimators (150 µm, 300 µm, 700 µm), depending on the element to be detected. The chosen instrumental parameters for each element are based on the recommended parameters proposed by Willis et al. [20]. The correction for inter-element matrix effects based on fundamental parameter models was used for the calibration of each element. The X-ray fluorescence spectrometer is calibrated for high- and low-alloyed steels (Mo, Al, Si, Cr, Mn, Ni, Cu, Sn), Cu alloys (Mg, Al, Si, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sn) and Al alloys (Mg, Si, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Sn), suitable to the three investigated matrices.

Figure 2. Employed S1 Titan 600 pXRF for the p/EDXRF analysis of metal alloys (left). The device was mostly operated in a radiation-safe, closed container, where the pXRF is mounted from underneath. The WDXRF experiments were conducted with an AxiosMAX device (right). Each 50 mm large alloy sample was placed in one steel cup, depicted on the left side of the image.

2.2.4. LIBS

For the LIBS analysis of the test alloys, the measurements were performed with the MopaLIBS system (Figure 3) and LIBS Software Suite (Secopta analytics GmbH, Teltow, Germany). For the measurements and analysis, the integrated application module Mopa Fast was used. For the analysis of different alloy classes, different data evaluation methods were installed on the system which contains the qualitative classification of main alloys, such as Cu-, Al-, Zn- and steel-base, as well as quantitative calibrations for aluminum and steel. The measurements were performed under room temperature and air conditions, and the MopaLIBS installed over a conveyer belt with tested speeds of 0.5 m/s, 1 m/s, and 2 m/s. The system has a distance sensor to obtain a height profile of the scrap, a cleaning laser, and a LIBS laser. The cleaning laser, also called pre-ablation laser, cleans the surface of the scraps and has a laser energy of 1 mJ, a repetition rate of 100 kHz, a spot size of approximately 100 µm and emits a wavelength of 1064 nm. The properties of the LIBS laser, which is used to generate the plasma, are similar to the pre-ablation laser with one exception: the repetition rate is 20 kHz. The spectrometer is coupled with a CCD-detector and has a wavelength of 240–420 nm, which is covering several atomic emission lines of the target elements. The resolution of the spectrometer is 0.09 nm. The measurement time for one measurement line is ca. 7 ms.
One challenge is the different shapes and heights of individual alloys and scrap pieces. Therefore, a dynamic focusing for an optimal laser alignment is favored, which can be achieved by a distance sensor. It was developed and demonstrated by Bohling et al. that the laser distance sensor of the MopaLIBS allows a dynamic focusing in a range of 140 mm, enabling the investigation of samples with different shapes and heights [21]. With the known sample height profile an optimal laser alignment on the sample surface is assured which provides good spectral data and allows to quantify even minor components.

For a robust calibration, partial least squares regression (PLSR) as a multivariate method has been used. At this system, a matrix-specific calibration for aluminum alloys and steels exists, but unfortunately no calibration for Cu alloys. Accordingly, only the three steels and the three Al test alloys were measured with this LIBS device.

3. Results
3.1. Spark-OES Validation

Three steels and three Al alloys were tested to prove the suitability of spark-OES for determining the correct chemical composition. A comparison of the values obtained by two spark-OES with the guaranteed values of the certified reference alloys (CRAs) is shown in Table 2. The uncertainties of the spark-OES measurements of the CRAs are calculated by using twice the standard deviation, \( s \), and are compared with the certified absolute errors.

In general, the spark-OES values are in good agreement with certified values for the CRAs. The absolute deviations of the matrix elements (Al, Fe, Cu) are below 0.3 wt.\% with the exception of the ZRM 297-1 sample, for which the Fe content is not certified and was only calculated to the residue of the sum of all other elements to 100 wt.\%. Such a procedure was applied to enable a better visualization of differences between certified and spark-OES values. However, a fully correct comparison can only be drawn if the Fe content is certified. For the concentration range from 1 wt.\% to 10 wt.\%, there are only relative deviations in the elemental composition of less than 5% of the value, though several spark-OES values show higher absolute deviation to the certified values than the 2s-range of measurement uncertainty. Notable examples are the Cu and Ni contents in different matrices and concentration ranges. The results from the spark-OES for the concentration range below 1 wt.\% exhibit that most relative deviations are lower than 10% of the certified values, exceptions being, for example, Al in the ZRM 192-1 steel or Ni in the BAM-311 Al alloy. Deviations of concentrations in the \( \mu g/g \)-range higher than the corresponding measurement uncertainties cannot be explained by the confined detection limit of the analysis technique itself. Commonly, commercial spark-OES devices are used to determine impurities in the 100 \( \mu g/g \)-range for most elements (with exceptions even in the 10 \( \mu g/g \)-range) and show similar or lower quantification limits than some of the certified
metal concentrations [22,23]. A reason could be the non-adequate calibration in the lower concentration range for Cu, Ni, Fe, etc. on the devices we employed for this study.

Table 2. Averaged elemental composition (in wt.%) of the used CRAs, determined by three (steels), four (Cu), or five (Al) individual spark-OES measurements, compared to the certified values, given by BAM. Only the results for several industry-relevant elements are shown. The BAM concentrations for Fe and Al as major elements (italic numbers) are not certified but have been calculated by assuming them as residual of all other elements to 100 wt.%. The last digits in brackets describe the level of the measurement uncertainty, expressed by 2 s. Non-matching spark-OES values are marked red.

| CRA         | Al     | Si      | Fe      | Cu      | Mn      | Mg      | Cr      | Ni      |
|-------------|--------|---------|---------|---------|---------|---------|---------|---------|
| ZRM 192-1   | 0.0308 | 0.219   | 96.806  | 0.0453  | 1.377   | -       | 0.0717  | 0.755   |
| Spark-OES   | 0.0188 | 0.223   | 96.968  | 0.0105  | 0.0615  | -       | 0.1737  | 12.09   |
| ZRM 284-3   | -      | 0.0442  | 67.937  | 0.089   | 0.089   | -       | 0.1750  | 12.10   |
| Spark-OES   | -      | 0.023   | 67.906  | <0.01   | 0.094   | -       | 0.1737  | 12.09   |
| ZRM 297-1   | 0.0195 | 0.344   | 66.226  | 0.204   | 0.897   | -       | 18.37   | 12.33   |
| Spark-OES   | 0.0116 | 0.381   | 68.160  | 0.182   | 0.866   | -       | 18.20   | 11.80   |
| EB 313      | 94.734 | 0.363   | 0.391   | 0.093   | 0.495   | 3.40    | 0.1224  | 0.0276  |
| Spark-OES   | 94.67  | 0.381   | 0.412   | 0.091   | 0.499   | 3.38    | 0.1292  | 0.0311  |
| BAM-311     | 91.68  | 0.057   | 0.310   | 4.653   | 0.694   | 1.56    | 0.1037  | 0.0519  |
| Spark-OES   | 91.59  | 0.077   | 0.316   | 4.801   | 0.668   | 1.64    | 0.1097  | 0.0649  |
| EB 315a     | 85.036 | 9.88    | 0.621   | 0.248   | 0.311   | 0.446   | 0.0274  | 0.0955  |
| Spark-OES   | 84.73  | 10.019  | 0.616   | 0.252   | 0.313   | 0.4795  | 0.0278  | 0.0922  |
| BAM-367     | -      | -       | 1.443   | 0.723   | 0.0347  | 9.72    |
| Spark-OES   | -      | -       | 1.320   | 0.645   | 0.052   | 9.71    |
| BAM-378     | -      | 0.0182  | 0.943   | -       | 0.0029  | 0.0018  |
| Spark-OES   | -      | 0.0180  | 0.931   | -       | 0.003   | 0.0061  |
| BAM-394a    | -      | 0.1232  | 0.576   | 0.0013  | -       | 0.0386  |
| Spark-OES   | -      | 0.125   | 0.573   | <0.001  | -       | 0.042   |

Since the relative differences between spark-OES and the certified values for concentrations >0.1 wt.% are below 10%, we assess the spark-OES to be employable as a technique, against which the results from LIBS, WDXRF, and EDXRF experiments can be benchmarked. Nonetheless, the deviations for these element-matrix combinations have to be regarded for the benchmarking as a potential source of error. That being investigated, in a second step spark-OES experiments with the nine test alloys were conducted, whose results are shown in Table 3.

Table 3. Mean average of the elemental composition (in wt.%) of the used test alloys, determined by three (steels), four (Cu), or five (Al) individual spark-OES measurements. Red marked values represent metal contents exceeding the limits given by the European standard specification (in Table S1). The measured average concentrations of Sn in the CuSn8 alloy is 7.79(28) wt.% and of Pb in CuZn39Pb3 is 3.27(15) wt.% Both values conform to the specifications. The last digits in brackets describe the level of the measurement uncertainty, expressed by 2 s.

| Alloy   | Al     | Si      | Fe      | Cu      | Mg      | Cr      | Ni      | Zn      |
|---------|--------|---------|---------|---------|---------|---------|---------|---------|
| A99.5   | 99.708 | 0.06    | 0.1845  | -       | -       | -       | -       | -       |
| AlMg4.5Mn | 94.883 | 0.082   | 0.273   | 0.020   | 4.097   | 0.074   | -       | -       |
| AlSi1MgMn | 96.709 | 1.142   | 0.212   | 0.032   | 0.854   | 0.150   | -       | -       |
| CuNi10Fe1Mn | -   | -       | 1.56    | 87.98   | -       | 9.68    | 0.021   | -       |
| CuZn39Pb3 | 0.0140 | 0.297   | 0.57    | 0.015   | 0.047   | 38.80   | -       | -       |
| CuSn8   | -      | -       | 91.83   | -       | -       | -       | -       | -       |
| X5CrNi18-10 | 0.0094 | 0.47    | 70.80   | 0.50    | 18.3    | 8.11    | -       | -       |
| 45NiCrMo | -      | 0.257   | 93.3    | 0.088   | 1.360   | 3.96    | -       | -       |
| 42CrMo4  | 0.0356 | 0.272   | 97.40   | 0.017   | 0.99    | 0.055   | -       | -       |

Most of the metal concentrations are within the specifications for the test alloys, given by the European standards (see Table S1 in the Supporting Information). Remarkably, even traces of several elements, such as Si and Ti in the µg/g-range, conform to the set limits, which reveals the general good quality control of the alloy manufacturers. However, some
spark-OES values exceed these limits, specifically the Cu contents of the high-alloyed steel and the 45NiCrMo steel. As demonstrated in the step before, the spark-OES showed also deviations for Cu and Ni in the certified steels (Table 2). Nonetheless, if a similar factor of deviation of the spark-OES to the ‘true’ value is assumed for the steels of the test samples, the limits given by the European standards are still exceeded for the case of copper. Thus the spark-OES measurements prove the contamination of the steels from the production with Cu. This behavior has been described in other studies as well, posing a problem for the production of new high-performance steels from scraps [24,25].

3.2. Method Comparison

3.2.1. EDXRF—Lateral Sample Homogeneity of Test Alloys

Having examined spark-OES for suitability as benchmarking technique, we investigated the spatial homogeneity of the elemental composition of the test alloys. Since this study aims to provide recommendations for application in the metal and recycling industry, we had to define a good balance between the spatial distance of the measurement spots and the efforts for the experiments. Sophisticated approaches, such as using an electron microprobe with micrometer resolution [26], need special sample preparation and consume too much time for scanning large sample areas, which hinders the practical analysis of metal contaminations in 2–50 cm large alloy or scrap pieces. For the spatial homogeneity tests, the handheld EDXRF technique was chosen which requires less sample preparation, shorter measurement times, but covers a comparably high probing area (4 mm, see Section 2.2.1). The information about the integrated composition stems from the sample volume excited by the X-rays within the 4 mm-wide circle. Spark-OES and WDXRF were not employed for this task, because their measurement spots are either too large (20 mm for the spark-OES) or need higher acquisition times (15 min per spot for WDXRF).

For the test, we followed the statistical procedure described by Fearn et al. previously [27,28]. There, a detailed explanation of the execution of such a test is given. Accordingly, each test alloy bar was cut into 15 equally sized pieces, whose surfaces were probed at two different random spots. For each spot, two subsequent measurements were performed to estimate the precision of the EDXRF instrument itself. Cochran’s C test served as a method for the detection of outliers in the data [29]. For simplification of data handling, the values, for which the EDXRF device registered a concentration below its internal limit of detection, were set to zero and not further regarded for the statistical evaluation. The sum of the squared differences between the two repeated measurements was calculated to determine the analytical variance of the method itself. Furthermore, the variance of the sums for each pair of repeated measurements was extracted from the data to obtain the sampling variance. Then, a tolerable sampling variance was estimated by using the center value of the European standard limits (e.g., an Fe content in Al99.5 of 0.2 wt.%). In the last step, the critical parameter was calculated, taking the analytical experimental variance and the tolerable sampling variance into account, and compared to the experimental sampling variance. If the latter exceeds this critical value, the alloy is for the targeted not homogeneous. We performed this test for the most relevant elements in each alloy and called a material homogeneous, if it is homogeneous for most of those elements.

A compressed statistical visualization (box plot) of the spatial homogeneity experiments is shown in Figure 4. For better readability, only the results for the main metals Al, Fe, Cu, and the important side element, S, are displayed. Test alloys, in which no concentrations of these elements were detected, are neglected. The coloring of the box hints at the accordance of the compositions determined by EDXRF with the European standard for each test alloy. Green boxes represent the conformity with the standards, with the second and third quartile of the measurement values (in the box) being within the given limits. Red boxes do not conform to the standard specifications because the central half of the measurement values exceed the limits partially, even though the arithmetical mean value can be within the limits. Grey-colored boxes represent detected concentrations of an element for which no limit was specifically set in the standards. Thus, these alloys can
have some additional elements which can either pose a contamination risk, reducing its functionality, or are negligible for their planned use.

Figure 4. Box plots of the element concentrations in the test alloys determined by EDXRF. The results from several alloys are compared for the detection of four elements, which represent the most important ones for metal recycling: aluminum (top, left), iron (top, right), copper (bottom, left), and silicon (bottom, right). The drawn lines represent the lower (dashed) and the upper (striped) limit, respectively, given by the European standards. Green boxes are within the limits, red boxes partially exceed them, meaning that the sample is not fully compliant to the actual standard specification. For grey boxes, no specification in the standard is given. Note the different y-scales in one plot.

In general, the detected absolute local variability for the elements in most alloy matrices is low. Usually, the center half of the measurement values span a corridor of less than 0.2 wt.%, exceeding the experimentally determined average precision of the employed EDXRF instrument (2 s < 0.1 wt.%) only slightly. The relative deviations of the concentrations can sum up in some matrices to 50% of the arithmetic mean value. Especially, for trace amounts below 0.5 wt.%, higher relative deviations are obtained which can be explained by the limit precision of the EDXRF device noticeable in this low concentration range. Besides the cases of Si in the low-alloyed steel 42CrMo4 and Al in the Al99.5 alloy, all-metal contents determined by EDXRF conform to the limits given by the European standards or are not listed therein. As a piece of practical advice, care should be taken with respect to the mentioned elements and alloys. When these are of
particular interest either the calibration has to be refined or other methods should be applied. Significant inhomogeneities of individual elements (in brackets) were observed in the alloys Al99.5 (Mg), 42CrMo4 (Si, Cu, Ni), and X5CrNi18-10 (Cu, Mo). It demonstrates that the steel samples are mostly affected by a spatially varying degree of contamination with Cu and other metals.

3.2.2. Comparison of LIBS, EDXRF, and WDXRF Concentrations for Test Alloys

Having confirmed the high spatial homogeneity in relation to the volume to be analyzed of the test alloys, we determined the elemental concentrations for all nine test alloys by employing EDXRF, WDXRF, and LIBS. Due to the amount of obtained data, the results of four selected elements (Al, Fe, Cu, and Si) in the different test alloys are given here. (Figure 5). A comprehensive list of all quantification results for the four analysis techniques is available in the Supporting Information (Table S2).

For most test alloys, the results of the elemental analysis for EDXRF, WDXRF, and LIBS fit to the benchmarking spark-OES dataset very well. Absolute deviations are below 1 wt.% for the main components, Al, Fe, and Cu, and below 0.25% for the minor elements (content < 2 wt.%). An exception is here the Al content in the alloy AlMg4.5Mn determined by EDXRF. Relative deviations are lower than 3% of the respective values for the main components and lower than 25% for several side elements as being visualized by the logarithmic scale (Al, Fe). Higher relative deviations are detected especially for Si in Al alloys and steels or Mn in the high-alloyed steel sample. For the case of Silicon, the LIBS results are in better accordance with the spark-OES values than the ones of both XRF techniques. In opposite, LIBS and WDXRF overestimate the Mn content in low-alloyed steels compared to the spark-OES value, to which the EDXRF deviates the least. However, all techniques overestimate the Mn content in the high-alloyed steel sample. Although the concentration range is fairly above the precision of the individual technique, the relative difference is up to 65% of the spark-OES result. Noticeably, the EDXRF value is the closest, while the WDXRF deviates the most. The reason for this behavior is not clear: both the WDXRF and EDXRF calibrations are based on few dozen standard steel samples with certified Mn values in the proper concentration range from 0.1–2 wt.%, allowing for an accurate Mn determination. Furthermore, no similar finding has been reported in the literature.

A further significant exception is the case of Mg in the Al alloy AlMg4.5Mn0.7, where the EDXRF values are ca. 2 wt.% (40% relative to the detected concentration) above the spark-OES result, demonstrating a clear misfit with respect to the other analytical techniques. Similar behavior is observed for the Al99.5 alloy with relative deviations of the EDXRF value from the spark-OES of 5000%, though on a much smaller absolute scale (0.196 wt.% vs. 0.004 wt.%). However, for the other Al alloy, the EDXRF value matches the spark-OES benchmark remarkably well, and is close to the WDXRF and LIBS results. As already shown by the EDXRF homogeneity tests, all techniques could detect copper contamination in all steels to a certain extent. Whereas WDXRF exhibits values closest to the spark-OES for the low-alloyed steels, EDXRF results are in best agreement with the spark-OES ones for the high-alloyed steel. Testing further low- and high-alloyed steels would help to clarify these tendencies, which cannot be explained satisfactorily so far. All methods determined an unintended Cu contamination in all steel samples. For low-alloyed steels, WDXRF showed the best performance compared to the spark-OES results, whereas the most accurate values for the high-alloyed steels were obtained by EDXRF.
Figure 5. Comparison of the element concentrations determined by EDXRF, WDXRF, LIBS, and spark-OES for the nine test alloys. The results are compared for the detection of four elements, which represent the most important ones for metal recycling: aluminum (top, left), iron (top, right), copper (middle, left), silicon (middle, right), manganese (bottom, left), and magnesium (bottom, right). Note the different y-scales in one plot, starting with a logarithmic division and continuing with a linear division after the break. For clarity, the error bars of each average value are omitted. The matrix metal concentration for LIBS and spark-OES was calculated by subtracting the sum of all quantified elements from 100 wt%.
4. Discussion

The results of the preliminary spark-OES experiments on the certified reference materials showed that we can use it as benchmarking method for the other investigated techniques. The homogeneity test by EDXRF proved that our approach of using non-referenced alloys for the comparison of analytical techniques is valid because, apart from a few exceptions (e.g., steels 42CrMo4 and X5CrNi18-10), these alloys with known concentration limits are sufficiently homogeneous. Especially for the case of Cu, Si, Ni, and Mo in the steels, we attribute the inhomogeneities to problems in the manufacturing process. The influence of the employed cutting saw, the only device that was in contact with the sample surfaces, can be excluded because no similar impurities were detected in the other alloys. Thus, we can compare various techniques with different measurement spot sizes for their accuracy in the quantification of the alloy compositions. For most cases, the deviations of EDXRF, WDXRF, and LIBS from the values of spark-OES were rather small, indicating a suitability of all methods for the detection of major and most minor elements. Only a few exceptions are observed where one or more methods cannot detect a specific element in a specific alloy matrix properly. Whereas the absolute deviations of the EDXRF, WDXRF, and LIBS results from the spark-OES benchmark are in the low wt.% range, relative deviations of higher than 100% of the measured spark-OES value occur. This held especially true for the low concentration range below 1 wt.%, where the effect of the precision for each method plays a stronger role and affects directly the detection limit of the method. In addition, the precision of the instrument influences the performance of the detection as well. Much attention has to be paid to the proper calibration of the targeted concentration range within a specific matrix (e.g., Ni in high-alloyed steels). If the response of the instrument to the analyte concentration is not linear anymore, false quantifications of unknown samples are produced during the routine analysis. The tolerable deviation for the selected analysis technique depends on the nature of the target element and the application for which the target alloy has to be produced or sorted. For example, if a low-alloyed steel, such as 42CrMo4 is produced and has to be assured that it conforms to the European specification, its silicon concentration has to be below 0.4 wt.%. If the manufacturer or recycler uses a commercially available portable EDXRF device, the test can fail, and a limit-exceeding Si content is observed. Thus, lower quality of the manufactured alloy is assumed which can limit the use to fewer applications and result in a remarkably (for this example up to 50%) lower selling price of the product. By choosing LIBS or WDXRF for analysis instead, a standard conformity is obtained, leading to a categorization of the produced alloy as 42CrMo4, with potential use in automotive applications. The selection of the appropriate technique to analyze is fundamental for accurate quality control and efficient sorting process.

For the analysis of light elements in light element matrices (e.g., Mg, Al, Si in Al alloys), LIBS experiments show a better performance compared to the X-ray techniques. This is in accordance with the findings of previous studies, which is demonstrated for handheld analyzers in [30]. The X-ray cross-sections for the light weight elements Mg, Al, and Si are comparatively low comprising an obstacle for a correct quantification by XRF. In addition, strong X-ray absorption by air and the polymer detector window diminish the received fluorescence intensity further. In comparison, LIBS ensures a more accurate analysis of these light elements and can, after proper calibration, also distinguish between individual classes of aluminum alloys, such as 5.xxx and 6.xxx. Remarkably, the LIBS results fit generally well to the spark-OES values, although the acquisition time (few ms) for this technique was the lowest of all used ones. Similar to spark-OES, LIBS can create high signal counts in a short time by intense excitation pulses. Nevertheless, the experiments also showed that LIBS deviates in some matrices noticeably, e.g., more than 35% relative to the spark-OES value for the high-alloyed steel. The reason for this remains unclear but could be attributed to a non-sufficient base of calibration samples in the respective concentration range. Furthermore, we used lower acquisition times for the LIBS experiments than for
Contamination of steels with copper, even a Cu content below 1 wt.%, is usually unwanted in certain steels because it can only be used in construction materials. Such a loss of variability of use leads to a downcycling for the original steel alloy and to an obstacle for an efficient circular economy of metals [24]. As the results demonstrate, all employed analysis techniques are able to detect these impurities, allowing them for the use in quality control both for recyclers and metal-producers. Here, the XRF methods obtained more accurate results than LIBS, caused by the comparably good X-ray cross-section and differentiability of Cu and Fe.

Besides the accurate quantification of the alloy composition, other operational-relevant parameters are also important for the evaluation of the performance of each individual analysis technique. A method, allowing for high throughput by in-line analysis, can be much more economic, if it still shows a reduced, but satisfactory accuracy adequate to the analytical task. Especially LIBS is used in conveyor belt systems, running at belt speeds of a few meters per second. Therefore, the whole measurement process must be on a time scale of a few hundred microseconds. Contrary, the XRF techniques need acquisition times of several seconds to minutes due to their lower signal count rate and, for WDXRF, the consecutively scanning of each individual element-specific detection angle to obtain a complete spectrum.

A further important aspect is the effort needed for the calibration and operation of the method. As we experienced, the number of calibration samples required for an accurate multi-metal LIBS or OES calibration is much higher than the amount of reference materials needed for an XRF analysis. Most probably, this can be attributed to the more complex physical processes of plasma generation, ablation, and relaxation, resulting in a manifold of emission lines (especially for steels). However, a better performance of a well-calibrated system can also justify the higher effort for establishing the calibration and the operation of the analysis technique, if an accurate determination of traces of contaminations is needed. This can only be balanced by an economic assessment tailored individually to the specific analysis/separation task, for example, the correct determination of Mg in an Al alloy to decide to which alloy class the scrap piece belongs. Furthermore, several national and international standards exist instructing about the correct application of specific analyte preparation and analysis techniques for certain metal alloys and scraps [31,32]. These are especially important for licensed laboratories and analysis departments of large recyclers but difficult to meet by non-optimized analysis systems and procedures in smaller recycling companies.

Regarding the alteration of the sample by the probing technique, clear differences between the X-ray methods and the OES methods can be seen. Whereas the first ones leave the metallic samples unaltered, the latter ones ablate the uppermost layers of the sample. The depth of the trace from the pre-ablation and LIBS laser depends on the material properties, laser properties, and velocity of the conveyor belt, ranging in our case in the order of 20–40 µm. With higher repetitions rates of the laser and lower speed of the conveyor belt, the depth is increasing. The surface damaging penetration of the OES techniques has the advantage to probe a fresh surface, which is especially useful for the investigation of surface-coated alloys, such as low-alloyed/rusty steels or galvanized Al alloys. An effective way of probing the three-dimensional averaged composition or test for impurities in depth of several millimeters are none of the studied methods. Potential alternative future approaches overcoming some of these limitations could be the prompt gamma neutron activation analysis (PGNAA) [33] or the spectrally-resolved X-ray computed tomography (XCT) [34].

The results presented for the nine different, relatively pure (not oxidized nor mixed with other alloys) and homogeneous test alloys can be linked to the examination of production (or prompt) scraps, whose compositions are known to some extent prior to analysis. They are not yet mixed with other scrap streams. Such production scraps are already analyzed by multifold sensors to a satisfactory level in the metal industry and can already be sorted with
high efficiency [4]. As discussed above, there exists no single analysis technique, enabling a fast, easy-to-handle, and accurate composition determination in all-metal alloy matrices. One promising path to meet these requirements is the intelligent combination of several different methods in one analysis workflow/system. Several such multi-sensor systems for the in-line analysis and sorting of scraps have been successfully introduced in the past years [35,36]. Nonetheless, mixed post-consumer scraps still remain a major challenge due to their oxidized/dusty surfaces and their complex multi-alloy composition. The evaluation of the suitability of the WDXRF, EDXRF, LIBS, and spark-OES is subject to a study, which is currently being investigated.

5. Conclusions

In this work, we compared the capabilities of four different, widely employed analytical techniques (two OES and two XRF methods) to determine the chemical compositions of several relatively pure metal alloys. Instead of using only certified reference materials as in studies presented before, we examined the four techniques with commercially available test alloys whose chemistry is not certified. This novel approach to the field of cross-method characterization is more comparable to the routine analysis and process control of alloy manufacturing and production scrap recycling, which deal with non-referenced materials. By using certified reference alloys, spark-OES was evaluated as a suitable method to benchmark the results from the EDXRF, WDXRF, and LIBS experiments. The actual technique comparison was performed for nine different, commercially available test alloys, representing the main three metal matrices in the recycling industry: Al, Cu, and steel. First, the lateral homogeneity at the macro scale of most alloys was proven by EDXRF measurements. Absolute deviations to the mean composition were generally lower than 0.2 wt.%. For several elements in the test alloys, e.g., Cu in all steel samples and Si in 42CrMo4, impurities were detected which exceed the given specifications or are not listed therein at all. The steels 42CrMo4 and X5CrNi18-10 exhibited remarkable inhomogeneities for some elements which are attributed to low-quality controlled manufacturing.

Second, the average elemental composition for all four techniques was compared. We showed that for most of the pure, homogeneous alloy samples all methods determined similar results, proving their good suitability for metal (impurity) detection. For some specific elements-matrix combinations, such as Si in steels and Cu in Al alloys, LIBS show more accurate results, whereas the XRF techniques exhibit better performances for the main metal quantification due to its direct quantification of that main element. Moreover, a discussion about the individual advantages and disadvantages for each method is given, taking further process-relevant indicators, such as acquisition speed, preparation effort, and calibration complexity into account.

This comparative study shall serve as a guide for the use and interpretation of these four techniques in the metal production and recycling industries, dealing with relatively pure, homogeneous alloys linkable to production scrap. The described methodology and the given discussion shall help in assessing results from individual techniques critically by taking their detection limits, their suitability for different element groups, and accuracy into account. Moreover, it shall encourage the use of multi-method alloy analysis in science and industrial praxis. In a second ongoing study, we will demonstrate the capabilities of the four techniques for composition quantification in post-consumer scraps, consisting of dusty, oxidized mixed alloy pieces.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/met11050736/s1, Table S1: Limits of the elemental composition (in weight percent) of the test alloys given by European standard specifications. Table S2: Comparison of element concentrations (in wt.%) determined by EDXRF, WDXRF, and LIBS for all test alloys.

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References

1. Fraunhofer Institute for Systems and Innovation Research, Öko-Institut. Methodology for the Free Allocation of Emission Allowances in the EU ETS Post 2012; Sector Report for the Iron and STEEL industry: Karlsruhe, Germany, 2009.
2. Moya, J.A.; Boulamati, A.; Slingerland, S.; van der Veen, R.; Gancheva, M.; Mostafa, N.Y. Laser Induced Breakdown Spectroscopy compared with conventional plasma optical emission techniques. Comparison of WDXRF and AAS. J. Anal. At. Spectrom. 2016, 31, 584–588. [CrossRef]
3. Bengtsson, A. Laser Induced Breakdown Spectroscopy compared with conventional plasma optical emission techniques for the analysis of metals—A review of applications and analytical performance. Spectrochim. Acta B 2017, 134, 123–132. [CrossRef]
4. Noll, R.; Fricke-Begemann, C.; Brunk, M.; Connenmann, S.; Meinhardt, C.; Scharun, M.; Sturm, V.; Makowe, J.; Gehlen, C. Laser-induced breakdown spectroscopy expands into industrial applications. Spectrochim Acta B 2014, 93, 41–51. [CrossRef]
5. Ahmed, N.; Ahmed, R.; Rafique, M.; Baig, M.M.A. A Comparative Study of Cu–Ni Alloy Using LIBS, LA-TOF, EDX, and XRF. Laser Part. Beams 2017, 35, 1–9. [CrossRef]
6. Willis, J.; Feather, C.; Turner, K. Guidelines for XRF Analysis; James Willis Consultants: Cape Town, South Africa, 2014; Volume 1.
7. Jochum, T.; Günther, J.-U.; Bohling, C. Material Analysis in Fast Industrial Processes by LIBS. Photonics Views 2019, 16, 56–59. [CrossRef]
22. Hemmerlin, M.; Meilland, R.; Falk, H.; Wintjens, P.; Paulard, L. Application of vacuum ultraviolet laser-induced breakdown spectrometry for steel analysis—Comparison with spark-optical emission spectrometry figures of merit. *Spectrochim. Acta B* **2001**, *56*, 661–669. [CrossRef]

23. Zhang, Y.; Jia, Y.; Chen, J.; Shen, X.; Liu, Y.; Zhao, L.; Li, D.; Han, P.; Xiao, Z.; Ma, H. Comparison of the Analytical Performances of Laser-Induced Breakdown Spectroscopy and Spark-OES. *ISIJ Internat.* **2014**, *54*, 136–140. [CrossRef]

24. Jin, H.; Mishra, B. Minimization of Copper Contamination in Steel Scrap. In *Energy Technology 2020: Recycling, Carbon Dioxide Management, and Other Technologies*; The Minerals, Metals & Materials Series; Chen, X., Ed.; Springer: Cham, Switzerland, 2020. [CrossRef]

25. Daehn, K. Copper Contamination in End-Of-Life Steel Recycling, Developing a New Strategy from Million-Tonnes to Milligrams. Ph.D. Thesis, Cambridge University, Cambridge UK, 20 July 2019.

26. Harries, D. Homogeneity Testing at the Micrometer Scale. *Micros. Today* **2017**, *25*, 28–35. [CrossRef]

27. Fearn, T.; Thompson, M.A. A new test for ‘sufficient homogeneity. *Analyst* **2001**, *126*, 1414–1417. [CrossRef] [PubMed]

28. Thompson, M. Test for ‘sufficient homogeneity’ in a reference material. In *AMC Technical Briefs*; The Analytical Methods Committee: London, UK, 2008; pp. 1–2.

29. Cochran, W.G. The distribution of the largest of a set of estimated variances as a fraction of their total. *Ann. Hum. Genet.* **1941**, *11*, 47–52. [CrossRef]

30. Senesi, G.S.; Harmon, R.S.; Hark, R.R. Field-portable and handheld laser-induced breakdown spectroscopy: Historical review, current status and future prospects. *Spectrochim. Acta B* **2021**, *175*, 106013. [CrossRef]

31. EN 14726:2019. In *Aluminium and Aluminium Alloys—Determination of the Chemical Composition of Aluminium and Aluminium Alloys by Spark Optical Emission Spectrometry*, German version; Beuth-Verlag: Berlin, Germany, 2019.

32. Swedish Institute for Standards. *X-ray Spectrometry—X-ray Emission and X-ray Fluorescence Analysis (XRF)—Part 2: Definitions and Basic Principles for Measurements, Calibration and Evaluation of Results; DIN 51418-2:2015-03*; Beuth-Verlag: Berlin, Germany, 2015.

33. Im, H.-J.; Song, K. Applications of Prompt Gamma Ray Neutron Activation Analysis: Detection of Illicit Materials. *Appl. Spectrosc. Rev.* **2009**, *44*, 317–334. [CrossRef]

34. Egan, C.; Jacques, S.; Wilson, M.; Veale, M.C.; Seller, P.; Beale, A.M.; Pattrick, R.A.D.; Withers, P.J.; Cernik, R.S. 3D chemical imaging in the laboratory by hyperspectral X-ray computed tomography. *Sci. Rep.* **2015**, *5*, 15979. [CrossRef]

35. Koyanaka, S.; Kobayashi, K. Automatic sorting of lightweight metal scrap by sensing apparent density and three-dimensional shape. *Resour. Conserv. Recy.* **2010**, *54*, 571–578. [CrossRef]

36. Braibant, L.; Leroy, S.; Barnabé, P.; Dislaire, G.; Pirard, E. Non-ferrous scrap metals classification by hyperspectral and multi-energy X-ray transmission imaging. In Proceedings of the 8th Sensor-Based Sorting and Control, Aachen, Germany, 8 March 2018; pp. 39–47.