Quantitative laser-based x-ray fluorescence and particle-induced x-ray emission

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Abstract
In this work, we demonstrate the feasibility of quantitative laser-based x-ray fluorescence (XRF) combined with particle-induced x-ray emission (PIXE) (called XPIF for x-ray and particle-induced fluorescence) spectroscopy analysis for elemental composition in solid samples. A multi-hundred TW laser system accelerated protons and produced x-rays that were impinging on solid samples, inducing characteristic line emissions of the elements contained in the material. The x-ray yield obtained from the characteristic emissions for each element can be related to its mass concentration using both the thick PIXE and thick XRF formalism. This is performed by using of an iterative numerical procedure. We tested the validity of our method on three homogeneous metallic materials, stainless steel, bronze and brass. The mass proportions of these samples retrieved by our analysis (XPIF) is within the errors bars compared with a commercial energy dispersive x-ray spectrometer.

1. Introduction

The production of secondary sources of charged particles or photons, as generated by the interaction of an intense laser pulse with matter, is a topic of large interest in particular since these laser-accelerated sources are very compact, have a high brilliance and are very versatile. In material science, the simultaneous production of ions, electrons and photons during the laser matter interaction can be used to induce element-specific x-ray emission for atomic elements identification or for quantitative analysis of elements within a material as the yield of characteristic x-ray is proportional to the element’s mass concentration. Standard techniques used to retrieve these information are x-ray fluorescence (XRF), particle-induced x-ray emission (PIXE) and energy dispersive x-ray (EDX) fluorescence. In addition, there is the laser-induced breakdown spectroscopy, however, compared to the previous spectroscopies, this analysis technique is destructive and therefore not suitable for analyses where the sample needs to be minimally damaged.

XRF is a technique that has been developed at the beginning of the twentieth century following the discovery of the x-ray radiation by W.C. Röntgen in 1895. To induce the XRF, the incident x-ray is typically produced by either an x-ray tube, a gamma ray source or a synchrotron accelerator. For quantitative analysis, it is important to characterize the x-ray source spectrum especially for x-ray tubes where the emitted radiation is composed not only of characteristic line emissions but also from continuous emission due to Bremsstrahlung radiation. The studied sample can be located in air and the probed thickness is around a few hundred microns. PIXE is a technique developed in the 70s that uses charged particles, usually protons, to induce element-specific x-ray emission for analysis of a sample. As such, PIXE allows retrieving a precise fingerprint of a material and, given its high sensitivity that reaches the parts-per-million, is employed as diagnostic for cultural heritage [1], biomedical [2] or environmental [3] applications. The drawback of this technique is that it requires large, complex and costly particle accelerators. Its use is therefore limited to the few existing facilities. It is possible to position the studied sample in air and the
Figure 1. (A) Experimental setup sketch showing the laser matter interaction in the vacuum chamber and the different detectors used to characterize the proton spectrum (time-of-flight (TOF) and Thompson parabola (TP)). The proton beam forms a diverging cone of 45° and the x-rays are emitted isotropically. (B) Picture of the experimental setup showing the position of the different detectors (TP with micro channel plate (MCP-TP), TOF diamond detector and the x-ray camera. (C) Zoom-in on the protons/x-rays interaction point with the sample, explaining the terms used in equations (1a) and (2a): the stopping power $S$ and attenuation coefficient $\mu$ composed of $i$ elements (illustrated in green and red dots) with compositions $c_i$ and cross sections $\sigma_{p,i}$, $\sigma_{x,i}$. The distances ($d_1$, $d_2$ and $d_3$) refer to the penetration depth of protons and x-rays described in equations (1a) and (2a), namely: the x-ray source entry depth $d_1 = \rho t \cos \theta_1$, the proton range $d_2 = \int dE S(E)$ and the exit distance of characteristic x-rays $d_3 = \int_{E_0}^{E} dE' S(E') \cos \theta_1 \cos \theta_2$ for PIXE or $d_3 = \rho t \cos \theta_2$ for XRF. (D) Proton spectrum $f_p(E)$ produced by a 5 μm Cu interaction target, as averaged over 10 shots.

The probed thickness is around a few tens of microns. It should be noted that XRF and PIXE are complementary in term of sensitivity that is function of the sample’s elemental composition. PIXE is more sensitive (resolution of up to a few tens of ppm) for light elements found in organic material [4]. EDX is used in scanning electron microscopy (SEM) and transmission electron microscopy. The studied sample must be kept under vacuum and the probed thickness is only a few micrometers. The first reported use of a laser produced source for fluorescence analysis is the work by Valle Brozas et al in 2016 where a laser beam incident on a solid Cu target at $\sim 10^{17}$ W cm$^{-2}$ produced x-rays and electrons for the study of pigments [5]. First experimental demonstration of laser-PIXE using laser-accelerated protons has been obtained in 2017 by Barberio et al [6].

In this experiment, the laser-acceleration was produced using the so-called target-normal sheath acceleration [7, 8]. This is the most routinely available acceleration mechanism, provides more reliability and stability for the accelerated particle and occurs when a high intensity short-pulse (duration $< 1$ ps) laser hits a solid target in the micrometric thickness range. During the ultra-intense laser interaction with the target, energetic electrons (‘hot electrons’) are pushed from the front surface of the target inside the target by the laser ponderomotive force. A certain number of electrons manage to escape at the rear target surface due to their high kinetic energy. However, some electrons are retained at the back surface of the target by the positively charged target bulk. This generates a strong (TV m$^{-1}$) electric field at the target rear surface interface which accelerates ions at the back surface of the foil, which is initially unperturbed. The ions are coming from hydrocarbon impurities and contaminants located on the back surface and stem out of the target almost normally, with a divergence angle of about 20° conical half-angle and a Maxwellian energy spectrum: typical laser-accelerated proton spectra range from very low energy protons (tens of keV) up to multi-MeV energy protons, where the maximum obtained proton energy scales with increasing laser-energy (for typical proton spectra, see figure 1(D)).

On commercial 100 TW range lasers, featuring laser energies of 2–5 J, maximum proton energies can reach about 10–20 MeV with an integrated number of protons of about $10^{11}$–$10^{12}$ per shot. These ions can be used to induce vacancies in the irradiated sample and produce x-ray emission. The energetic electrons escaping the target, which are polyenergetic and can reach energies up to 10 MeV, can be used for EDX analysis [9]. The electrons remaining inside the target can produce both characteristic line emission and Bremsstrahlung radiation while they propagate, radiation which can be used for XRF analysis. The x-ray radiation emission can be considered as isotropic. Theoretical studies have shown that the fluorescence conversion efficiency (protons-to-x-rays) is about $10^6$ protons for one single x-ray photon [10, 11], although this number depends on the material and proton energy.
The simultaneous production of different types of particles and radiation, as obtained in the laser–matter interaction process, enables the combination of different characterization techniques (PIXE, XRF, EDX, x-ray and proton-induced fluorescence (XPIF)), thus improving material analysis diagnostics. However, these laser-generated secondary sources are very peculiar since they produce multiple broadband sources, concomitantly. While a qualitative analysis of elements within the materials is easy in the case of monoenergetic particle sources (e.g. in a conventional EDX or PIXE facility), the broadband spectra of laser-generated sources make a quantitative analysis much more complex. Depending on the particle type and its energy, fluorescence x-ray photons can be produced at various thicknesses within the material to be sampled. However, these photons need to cross the material in order to reach the detector and the deeper in the material the photons are produced, the more they will be attenuated. Electrons deposit their energy at the surface, while x-rays are absorbed all along their propagation path and deeper in the material. Protons deposit most of their energy at the end of their motion (Bragg peak), where they produce most of the x-rays. In addition, in laser-PIXE, protons with different energies are impinging at the same time: the photons detected by the detectors can therefore been produced at different depths and by protons with a variety of energies. In any case, quantitative analysis requires solving complex equations and a good knowledge of the source.

In this paper, we demonstrate that laser-accelerated sources using a combination of ions and x-rays, corresponding to the technique XPIF, can be used for the quantitative analysis of elements within a material. We confirm this by comparing quantitative analysis using different calibrated samples that have been benchmarked against a commercial EDX spectrometer.

2. Methodology

2.1. Experimental setup

The experimental setup and a picture of it are shown respectively in figures 1(A) and (B). The setup is similar to the one used in Puyuelo-Valdes et al [12] in which it was demonstrated that ultra-intense laser–matter interaction produces a versatile, non-destructive, fast analysis technique that allows to switch from laser-driven PIXE to laser-driven XRF, or to apply both techniques simultaneously, by simply varying the atomic number of the proton source target. This technique was named laser-based XPIF.

We used the laser-based ion acceleration beamline located on the 100 TW Ti:Sapphire ALLS laser facility (Varennes, Canada) to produce light pulses with an energy of 2.2 J after compression (central wavelength \( \lambda_0 = 800 \) nm) and a pulse duration of 22 fs at Full-Width-Half-Maximum (FWHM). The p-polarized 100 mm (at \( e^{-2} \)) laser beam was focused down by an \( f/3 \) off-axis parabola at an angle of 20° with respect to target-normal, down to a 5 \( \mu \)m diameter spot (FWHM), producing an on-target intensity of about 1.3 \( \times \) 10^{20} W cm^{-2} under high-vacuum conditions (<10^{-6} mbar). As interaction targets, we used foils of 5 \( \mu \)m copper (Z = 29, purity 99.9%).

The material sample was positioned at a distance of 75 cm on the 0° (proton) axis, inside a small aluminum chamber that was connected to the main experimental chamber using a tube. A close-up showing the protons/x-rays interaction geometry with the sample is presented in figure 1(C). The angle of the sample, with reference to the proton axis (0° axis), was 45°. Two magnets producing a 0.1 T magnetic field were positioned on the 0° axis at a distance of 20 cm from the source, in order to deflect the co-moving electrons without modifying the proton energy distribution at 0°. The proton beam had a diameter of 3.8 cm in the center of the auxiliary chamber, where the samples were placed. To avoid any interaction between the laser-based sources and the KF40 tube that connects the main chamber with the auxiliary chamber, producing an undesired XPIF signal within our detector, a collimator of diameter 2.54 cm was placed at a distance of 50 cm from the interaction target. A typical proton spectrum, as obtained during the experiment, is shown in figure 1(D).

A PI LCX:1300 x-ray camera cooled with liquid nitrogen (1300 \( \times \) 1340 pixels of 20 \( \mu \)m encoded in 16 bits grayscale) was placed at a distance of 8 cm from the sample and at 90° with respect to the 0° proton axis to diagnose the x-rays. The detector had a usable quantum efficiency range from about 2.2 keV to 20 keV for retrieving x-ray photon spectra by single photon counting. The Fano-limited resolution formulation [13] gives a resolution of about 0.2 keV for 8 keV. We verified the calibration of the camera by measuring x-rays produced by Ca (\( K_x = 3.69 \) keV and \( K_\beta = 4.01 \) keV), up to Ag (\( K_x = 22.16 \) keV and \( K_\beta = 24.94 \) keV). To minimize the effect of strong electromagnetic pollution produced as a result of the laser–matter interaction [14], we placed the x-ray camera outside the main chamber, shielded with lead bricks and far from the laser interaction point.

A 250 \( \mu \)m-thick Be window of diameter 5.08 cm, which allows the transmission of 90% of x-rays with 8 keV energy, was used to keep the camera in vacuum, protect it from visible light and reduce the
background signal. At each shot, the CCD recorded images of the obtained x-ray spectrum. The camera’s intensity values were calibrated to the x-ray photon energy by linear regression using the $K_{\alpha}$’s of the following elements: Ti (4.51 keV), Ni (7.48 keV), Cu (8.05 keV), Zn (8.64 keV), Nb (16.62 keV), Mo (17.48 keV) and Ag (22.16 keV). The $K_{\alpha}$ photons were produced by irradiation of a sample with purity 99.99% with the proton and x-ray source. The resulting slope of 0.01413 ± 0.00005 (keV/counts) and origin intercept 0.07 ± 0.05 keV yields an uncertainty of about 0.05 keV which is below the energy resolution of 0.2 keV. Precise identification of elements using $K_{\alpha}$ is thus possible with this camera. The method to evaluate the contribution of both the protons and the x-rays is detailed in the next section.

2.2. Photon yield obtained by PIXE

The yield $Y_{p,i}$ of the element $i$ produced by protons can be related to the mass proportions $c_i$ with the thick sample PIXE formalism [11] adapted for a broad-band distribution of protons $f_p(E) = \frac{d^2N}{dx dt}$ (see figure 1(C)):

$$Y_{p,i} = \frac{\Omega}{4\pi} N_A M_i c_i \int_{E_0}^{E_i} f_p(E) \int_{E_p}^{E_i} \sigma_i(E) \omega_i T_i(E) \frac{dE}{S(E)} \frac{dE}{dE_p},$$  \hspace{1cm} (1a)

$$T_i(E) = e^{-\mu_i(E_p) \int_{E_p}^{E} \mu(E) \frac{dE}{dE_p} \cos \theta \cos \theta_2}, \hspace{1cm} (1b)$$

where $\Omega$ is the solid angle subtended by the sample, $N_A$ is Avogadro’s constant and $M_i$ the molar mass. A proton of energy $E_0$ is incident on the sample and loses its energy during its trajectory within the sample. When the proton reaches the energy $E_i$, it generates a number of $K$-shell fluorescence photons per energy and per solid angle proportional to $\sigma_i(E) \omega_i T_i(E) \frac{dE}{S(E)}$ where, $\sigma_i$ is the ionization cross section for protons tabulated in the work of Pia et al [15] calculated using the plane wave born approximation and Energy-loss Coulomb-Repulsion Perturbed-Stationary-State Relativistic (ECPRSSR) theory [16], $\omega_i$ is the fluorescence yield tabulated in [17], $S(E)$ is the compound proton stopping power (found using SRIM [18]) computed using Bragg’s additivity rule [19] and $T_i(E)$, given by equation (1a), is the attenuation of the emitted photons across the sample. The number of x-rays emitted by the proton is integrated along its course from its initial energy $E_0$ down to full stopping of the proton, assuming a thick sample approximation, i.e. the proton is fully stopped in the material. This quantity, the integrated number of x-rays emitted by the protons, is then integrated over the entire proton spectrum ranging from the minimum energy $E_0$ up to the maximum $E_i$. In equation (1b), $\mu_i$ is the proton mass attenuation coefficient tabulated in the NIST-XCOM database [20] and $\theta$ and $\theta_2$ are respectively the incident angle of the protons and the output angle of the photons. The compound attenuation coefficient is computed by $\mu = \sum_i c_i \mu_i$ as described in [19] evaluated for the characteristic energy line of the element $i$.

2.3. Photon yield obtained by XRF

To quantify the contributions of x-rays to the integrated photon yield, the XRF formalism for thick samples is employed [21]. In our case, when using copper as laser–matter interaction target, the x-ray excitation source consists of the Cu K$_\alpha$ and Cu K$_\beta$ with an energy of respectively $h\nu_{K_\alpha} = 8.05$ keV et $h\nu_{K_\beta} = 8.91$ keV. It is known that a higher Z material such as copper produces hard x-ray Bremsstrahlung radiation following a Maxwellian distribution $(dN/dE \sim \exp(-E/T_{\text{heat}}))$ [22] when interacting with a high-intensity laser. The hot electron temperature $T_{\text{heat}}$ is estimated to ~500 keV with our laser intensity of about $1.3 \times 10^{20}$ W cm$^{-2}$. In the work of Jarrott et al [23], the integrated count of Bremsstrahlung (from 1 keV to 100 MeV) is about the same order of magnitude as the $K_{\alpha}$ yield. However, the XRF cross section $\sigma_{j}(h\nu)$ from equation (2a) is approximately 1000 times smaller at 200 keV than at 10 keV for copper [17]. As a first approximation, the hard x-ray Bremsstrahlung was thus neglected in the x-ray spectra source for the XRF calculations.

According to [21], the yield $Y_{j,i}$ for the element $i$ of a sample constituted of $n$ elements can be expressed as:

$$Y_{j,i} = \frac{\Omega}{4\pi} N_A \sum_{j} \frac{c_i}{M_i} \left[ N_{K_\alpha} \sigma_{j}(h\nu_{K_\alpha}) T(h\nu_{K_\alpha}) + N_{K_\beta} \sigma_{j}(h\nu_{K_\beta}) T(h\nu_{K_\beta}) \right], \hspace{1cm} (2a)$$

$$T(h\nu_{K_\alpha}) = \frac{1 - e^{-\frac{\mu_{K_\alpha}}{\cos \theta_1} + \frac{\mu_{K_\alpha}}{\cos \theta_2} \mu_{K_\beta}}}{\cos \theta_1 + \frac{\mu_{K_\alpha}}{\cos \theta_2}}, \hspace{1cm} (2b)$$

$$T(h\nu_{K_\beta}) = \frac{1 - e^{-\frac{\mu_{K_\beta}}{\cos \theta_1} + \frac{\mu_{K_\beta}}{\cos \theta_2} \mu_{K_\alpha}}}{\cos \theta_1 + \frac{\mu_{K_\beta}}{\cos \theta_2}}, \hspace{1cm} (2c)$$
where $N_{K_{α,β}}$ is the number of x-rays of the source ($N_{K_{α}} = 4.3 \pm 1.1 \times 10^{10}$ and $N_{K_{β}} = 0.6 \pm 0.2 \times 10^{10}$ photons sr$^{-1}$) [12], $\sigma_i$ is the XRF cross section for production of $K_i$ radiation of the element $i$ tabulated in the work of del Rio et al. [17], $\mu_1$ and $\mu_2$ are respectively the compound x-ray mass attenuation coefficient at the source energy ($h\nu_{K_{α}}$) and at the emission energy of the $K_{α}$ line $i$ in the sample, $\rho$ is the density of the sample and $t$ is the material thickness. The coefficient $T(h\nu)$ in equations (2b) and (2c) accounts for the attenuation of the incoming x-rays and the emitted x-rays. The factor $T(h\nu)$ results from the integration of Beer–Lambert’s law over the sample’s thickness [21], which assumes uniformity of the sample’s composition with depth. It is important to note that only elements for which the K-shell binding energy is smaller than the energy of the x-ray source (in this case we were using a Cu proton target thus corresponding to a Cu $K_{α}$ line at 8.04 keV) can emit characteristic radiation. Therefore, when using a Cu laser target, only elements with an atomic number lower or equal to nickel are affected by XRF since nickel has a K-shell binding energy of 8.33 keV [17].

Using equations (1a) and (2a), the theoretical total photon yield $Y_{th} = Y_{X,i} + Y_{p,i}$ from both sources (PIXE and XRF) can then be computed for a given set of $c_i$ identified in equations (1a) and (2a), which are currently unknown. Equations (1a) and (2a) are nonlinear in $c_i$ since the stopping power and x-ray attenuation data depend on $c_i$, and this term appears in an exponential and integral ((1a) and (1b)). Therefore, one way to find the mass proportions is to proceed by an iterative way, i.e. to compare the yield $Y$ experimentally obtained from the spectrum to the simulated yield $Y_{th}$ and find the set of $c_i$ which best fits the experimental data. A homogeneous proportion for all $c_i$ (e.g. a two-element compound is attributed $c_1 = c_2 = 0.5$) is chosen as a starting point for the first iteration, and the $c_i$ are varied in each iteration until the best fit is obtained. We used a standard $\chi^2$ parameter in the iterative process [24] defined as

$$\chi^2 = \sum_i \frac{(y_i - y_{th,i})^2}{y_i},$$

(3)
to compare the yields from the spectra and the theoretical yield calculated at each iterations. The normalized yield $y_i = \sum_j y_{i,j}$ is used as an input to perform the optimization. The minimization of $\chi^2$ was carried out with the MATLAB® function fmincon with the constraint $\sum_i c_i < 1$ to take into account the undetectable smaller Z elements producing an emission energy below the detection range of the CCD. This minimization outputs the new set of $c_i$ for the studied sample along with the final simulated yields. The minimization routine ends when the difference between two $\chi^2$ values from two consecutive steps drops below $1 \times 10^{-10}$ (value that we chose, producing sufficient precision).

2.4. Numerical analysis

To retrieve the quantitative composition of elements when using laser-based x-rays and protons, the following procedure was implemented: the first step consists in extracting the x-ray emission spectrum from the raw image. A single pixel event (SPE) algorithm is applied to the CCD grayscale image matrix $A$ as described in the work of Fourment et al. [25] and Fourmaux et al. [26]. This algorithm, corresponding to one photon hitting a single pixel, is applied to the direct neighboring pixels ($3 \times 3$ cluster) of a given $(i,j)$ pixel of intensity $A_{ij}$ using a threshold of $3\sigma$:

$$A_{i+1,j} + A_{i-1,j} + A_{i,j+1} + A_{i,j-1} < 2 (A_0 + 3\sigma),$$

(4)
where $A_0$ and $\sigma$ respectively denote the mean value and the standard deviation of a reference image containing no x-ray signal. Indeed, we only consider the direct neighboring pixels, since adding the pixels at the extreme (e.g. $A_{i+1,j+1}$) contributes only very little (<1%) to the computation. The value of a pixel $A_{ij}$ must be greater than the background ($A_0 + 3\sigma$) to be considered in equation (4). This pixel filtering algorithm is illustrated in figure 2(A): in the red box, only the two photon impacts which had enough energy to overcome the background and were not directly next to another illuminated pixel were selected as a valid SPE.

This image processing method yields an increased photon energy resolution compared to other algorithms [25]. An improvement in the resolution comes at the cost of decreasing the quality of the photon statistics since the number of photon-hit events used to construct the spectrum is reduced by applying equation (4). Using the filtered array image containing only single pixel events, the grayscale values in raw x-ray spectrum $dN/dE$ can be built and converted to energy values using the calibration described in section 2.1. Equation (5), taken from [26], transforms the raw x-ray spectrum $dN_{SPE}/dE$ obtained with the SPE algorithm into a x-ray spectrum with absolute values $dN/dE(\mathcal{E})$:

$$\frac{dN}{d\mathcal{E}} = \frac{a}{k(E)\text{QE}(\mathcal{E})T(\mathcal{E})\Omega_{\mathcal{E}}} \frac{dN_{SPE}}{d\mathcal{E}},$$

(5)
where $k_1(\mathcal{E})$ is the probability of a SPE detected from one photon, $QE(\mathcal{E})$ is the quantum efficiency of the CCD, $T(\mathcal{E})$ is the transmission factor of the beryllium filter, $\Omega_c = 0.103 \text{ sr}$ is the solid angle of the camera in our experimental setup and $a$ is a dimensionless parameter that ensures the number of SPE counts is equal to the total count of photon events, typically ranging between 1 and 3.

Once the spectrum has been obtained, each peak in the spectrum has to be mapped to its corresponding characteristic x-ray emission line, taking into account that there could be some background noise (see figure 2(B) and related discussion later). A first source of error is the possibility that some characteristic x-ray lines of elements are very close or even overlap when the studied sample contains multiple elements, for which their energy lines are overlapping within the energy resolution of the camera [19]. For instance, the difference between the lines of Cr $K_{\beta}$ located at 5.95 keV and the Mn $K_{\alpha}$ located 5.90 keV [17] is below the energy resolution of the detector and both lines can thus be easily mistaken. Secondly, spurious responses from the detector such as escape peaks and pile-up events can also lead to misinterpretation of the peaks when applying the fitting routine (see figures 2(C) and (D)). An escape peak is a secondary excitation of the detector into itself: an incoming photon of energy $h\nu$ might have sufficient energy to ionize the silicon core electrons contained in the detector and generate a x-ray characteristic emission at 1.7 keV. The camera’s pixel therefore sees an effective energy $h\nu - 1.7 \text{ keV}$ [19]. In contrast, a pile-up event occurs when two photons (or more) of same energy hit the same pixel. Two photons hitting the same pixel appear as a peak located at twice its energy [19]. Again, this pile-up event can be misinterpreted as another element which is not truly present in the sample. Additionally, the x-rays generated by the laser–matter interaction can undergo Rayleigh scattering on the studied sample [12] and then be collected by the camera. For example, the Cu peak observed in figure 2(D) could be misinterpreted as a trace of copper in the sample, while the signal is due to Rayleigh scattering produced by the copper proton-producing target.

After the identification is completed, i.e. every peak is linked to the characteristic corresponding energy line of a specific element, a Gaussian-shape [19] envelope around the peak is produced to integrate the peak and retrieve the total integrated photon yield $Y_i$ associated to the x-ray line $i$ in the spectrum. The peaks were fitted using non-linear-least-squares fitting with 68% confidence interval bounds as uncertainty on the fit parameters (standard error of $1\sigma$). The background $B$ underneath the peaks was similarly integrated.
Table 1. Geometrical specifications of the studied samples.

| Sample       | Thickness (mm) | Surface area (cm²) |
|--------------|----------------|--------------------|
| Stainless steel | 1.54          | 30                 |
| Bronze       | 4              | 5.39               |
| Brass        | 0.5            | 25                 |

within $3\sigma$ to define a minimum detection limit (MDL) as typically defined: $\text{MDL} = 3\sqrt{B}$ [19]. If the sum of the integrated counts of a peak is lower than the MDL, it cannot be statistically associated to an element, but only as random noise (see figures 2(B) and (C)). When spurious responses are present in the signal, the integrated yield corresponding to these events (escape peaks and pile-up) must be added to its corresponding lines: for a pile-up event, the yield must be multiplied by the number of photon hits on the pixel. For instance, the yield of a double-count event related to a given line must be doubled before being added to the yield of its associated line. In order to automate the identification of peaks by taking into account all the aforementioned cautions, the following steps were implemented in the x-ray spectrum processing MATLAB® routine:

(a) Find the closest match between the peaks and the tabulated characteristic x-ray lines.
(b) If a $K_\beta$ line is found, verify the existence of its corresponding $K_\alpha$ line and confirm that the yields $Y_{K_\beta} < Y_{K_\alpha}$ since the emission probability of the $K_\alpha$ is greater than the emission probability related to the $K_\beta$ [19].
(c) Verify the presence of a pile-up event by seeking a match for a high-yield line with a peak located at twice its energy. A high-yield peak has a greater probability to produce a pile-up event.
(d) Eliminate the peaks with an integrated yield smaller than the MDL.

To speed up and ease the matching process between peaks and characteristic lines, only the common elements with energy lying within the camera detection range of 2–25 keV were analyzed, namely: $Z = \{14–20, 22, 24–33\}$. Scandium ($Z = 21$) and vanadium ($Z = 23$) were not considered because they were very unlikely to be present in the studied samples and could lead to erroneous identification of lines in the spectrum.

The final step is to relate the integrated count of each previously identified element to its elemental concentration in the sample, making use of the fundamental parameter method (FPM) [19]. This approach relies on a theoretical formulation based on radiation physics (shown in equations (1a) and (2a)). It is less precise than other empirical methods such as the internal standardization [19] method, based on known reference element (standards). However, it allows analysis of completely unknown samples and is useful for investigations in an explorative phase [21]. Hence, FPM allows obtaining a first approximation of the sample’s characteristic x-ray yield with the laser-XPIF setup. In order to perform the quantitative mass calculations of a sample with $n$ elements, one needs to consider $nK_\alpha$ lines with integrated yield $Y_i$ for the element $i$. Even though in our approach the $K_\beta$ lines were detected in order to avoid mistaken identification due to elemental overlap, only the information on the $K_\alpha$ lines is sufficient to complete the analysis. The set of $K_\alpha$ yields provide a sufficient number of parameters to perform the mass ratio computation. Higher order fluorescence is neglected in both calculations [21] because of its small impact (0–15% error on the results) compared to our 15% and 25% error on the proton and x-ray sources quantitative spectra.

3. Results and discussion

We restricted our study to three multi-element metallic samples in the same experimental configuration. The choice of metallic samples guaranteed a very homogeneous composition of the elements over a large surface area proton beam of several cm². Moreover, the samples have been chosen such as to have their x-ray emission lines in the detectable energy range of the camera. The different elemental composition complexity of the chosen materials also allowed to properly test and validate the numerical algorithm. Table 1 presents the important parameters used in the calculations.

3.1. Yield analysis

As a first step, the XRF spectra were measured for the samples in table 1, and were then processed according to the steps described in section 2.4. The spectra for brass and stainless steel are respectively shown in figures 2(C) and (D). The post-processing allowed us to measure the characteristic x-ray yields from the elements in the probed samples as shown in table 2.
Table 2. Measured yields on the x-ray spectra. The errorbar for element Ca is high due to a low signal to noise ratio in the x-ray spectra (see figure 2).

| Sample      | Element | $Y$ (counts) | $y$ (n.u.) |
|-------------|---------|--------------|------------|
| Stainless steel | Ca      | 88 ± 76      | 0.011 ± 0.01 |
|              | Cr      | 1722 ± 88    | 0.21 ± 0.01  |
|              | Fe      | 6582 ± 225   | 0.77 ± 0.03  |
|              | Ni      | 124 ± 7      | 0.015 ± 0.001 |
| Bronze      | Fe      | 403 ± 13     | 0.39 ± 0.01  |
|              | Ca      | 606 ± 11     | 0.60 ± 0.01  |
| Brass       | Cu      | 1069 ± 21    | 0.77 ± 0.01  |
|              | Zn      | 322 ± 15     | 0.13 ± 0.01  |

Figure 3. Comparison between the measured yield from the spectra and the simulated yield as obtained from the optimization procedure. We observe a very good agreement between these two quantities.

Table 3. Fit data: $T$ is the computation time for the fit using a laptop computer equipped with a 8th generation Intel Core i7 processor with 8 Gb of RAM, $\chi^2$ is the goodness of fit parameter from equation (3), $\eta = \frac{Y_{\text{sim}}}{Y_{\text{exp}}}$ is the ratio between the yield generated by XRF and by PIXE.

| Samples     | $T$ (s) | $\chi^2 \times 10^{-12}$ | $\eta$ (n.u.) |
|-------------|---------|--------------------------|---------------|
| Stainless steel | 41      | 1.08                     | 12.8          |
| Bronze      | 10      | 107                      | 23.5          |
| Brass       | 6       | 0.93                     | 0             |

The measured yields $Y$ were normalized ($y$) before being used as inputs in our $\chi^2$ minimization MATLAB® routine because the $\chi^2$ parameter defined in equation (3) compares the normalized simulated yield with the normalized measured yield to find the optimal set of mass ratios $c_i$. This set of normalized yields can be useful for uncertainty calculations or to quantify the quality of the fit between the experimental and simulated values as illustrated in figure 3. As mentioned in section 2.4, the measured relative yields from table 2 are input in the iterative MATLAB® routine. Varying the mass ratios $c_i$ at each iterations, the routine computes the relative simulated yield $y_i^{\text{th}}$ and finds the set of $c_i$ that optimizes the fit between $y_i$ and $y_i^{\text{th}}$. The final best fit at the end of the minimization process is displayed in figure 3 for the considered samples. The simulated and measured yields are in excellent agreement for every sample (as can be seen by the low values of $\chi^2$ for all elements—see table 3), which demonstrates that the iterative routine found the best possible set of $c_i$ for the experimental data: $y_i^{\text{th}}$ and $y_i$.

Furthermore, other information can be extracted from the results of the MATLAB® routine, such as the total processing time, the $\chi^2$ parameter between the simulated and experimental yields defined in...
equation (3) and the contribution to the global x-ray yield as induced by x-rays and protons: \[ \eta = \frac{Y_{X,i}}{Y_{p,i}}, \] i.e. the ratio \( \eta \) allows us to compare the contribution of XRF and PIXE in the total yield. If \( \eta > 1 \), most of the x-ray production measured by the spectrometer comes from the XRF and vice versa. Table 3 shows these parameters for every sample.

Even if the analysis is relatively complex because of the non-linearities in equations (1a) and (2a), the results are obtained rapidly (within seconds), which enables a fast analysis of multiple samples. The ratios \( \eta \) are consistent with previous experimental evidence in similar conditions and for these samples, the yield from XRF \( Y_{X,i} \) is about 20\( \times \) higher than the yield from PIXE \( Y_{p,i} \) (see figure 3 in Puyuelo-Valdes et al [12]).

### 3.2. XPIF benchmark with EDX

In order to validate our XPIF quantitative analysis technique, we benchmarked it with conventional EDX spectroscopy as obtained in conjunction with SEM. The energy range of the EDX detector ranged from 0.1 keV to 15 keV allowing to detect lower \( K_{\alpha} \) energy elements such as carbon and oxygen that are undetectable with our system. Figure 4 shows the XPIF concentrations as obtained using a measured proton and photon spectra within its errorbars. We present only the constituents visible by both XPIF and EDX, whereas other elements of lower atomic number \( Z \) detected solely by EDX are not displayed. For the three samples, the XPIF concentrations are in good agreement with the EDX analysis, all the values are within the errorbars. Brass is the sample for which the composition determined with XPIF was in the best agreement with the EDX analysis values.

The uncertainties on the element concentrations and the simulated yields observed in figures 3 and 4 are mainly due to the high uncertainty on the source spectra, namely 15\% for the proton spectrum and 25\% for the number of x-rays. The uncertainties for the brass sample are much smaller than for the other samples because only PIXE can induce x-ray emission: copper and zinc have a binding energy that is higher than the Cu \( K_{\alpha} \) and therefore are not affected by the x-rays produced by the laser–matter interaction (see explanation in [12]). The uncertainties on the set of \( c_i \) for brass consist of only uncertainties related to the experimental yields values deduced from the spectrum and the Gaussian fit. The uncertainty on the other geometrical experimental parameters: \( \Omega_d, \theta_1, \theta_2, t \) from equations (1a), (2a) and (5) are small (less than 1\%) compared to the source uncertainties and were thus neglected for the uncertainty calculations. All the radiation physics quantities such as the proton stopping power, cross sections and attenuation values were considered as exact values, since their uncertainty is negligible (less than 4\% for the stopping power [18]) compared to the proton and x-rays uncertainties. To evaluate the uncertainty on the sample’s composition, after the iterative process was completed, the error on the protons and x-rays sources was summed in quadrature to the error on the measured yields \( Y_i \) (obtained with the standard deviation (\( \sigma \)) from a Gaussian fit). As observed in figure 4, our XPIF method allows determining the elementary composition of materials with an acceptable uncertainty level. In figure 2(C), the peaks are well resolved and the uncertainty on the Gaussian fit is small (typically less than 5\%) compared to the excitation sources uncertainties. As discussed previously, when using the XPIF technique, a precise description of both proton concentrations is obtained.

![Figure 4. Comparison between the XPIF analysis and EDX analysis for the concentrations of the samples described in table 1.](image)
and x-ray photon numbers is needed, as they are the most influential parameters on the resulting calculated uncertainty. A precise value can be obtained by measuring simultaneously the proton spectrum, the number of x-rays and the characteristic emission spectrum from the sample. Another possibility is to extend the analysis over multiple laser shots to improve the statistical uncertainty.

To further verify the consistency of our code, we adapted the MATLAB® routine used for the PIXE quantitative analysis (which includes the yield computation and fitting procedure) for classical EDX analysis (which is based on impinging monoenergetic electrons), to verify the validity of the code and radiation physics data (stopping power, cross sections and attenuation coefficients). To do so, we adapted the source parameters to the EDX source and we modified equation (1a) to take into account the electron cross section tabulated in [27] and stopping power for electrons [28]. The electron flux employed in the EDX analysis is monoenergetic at 15 keV. Therefore, the large distribution $f_p(E)$ in equation (1a) is substituted with a Dirac delta distribution centered at 15 keV $f_p(E) = \delta(E - 15 \text{ keV})$. The same iterative procedure as described in section 2.4 was employed to retrieve the mass ratios. The concentrations $c_{\text{i,th}}$ obtained in this manner are in agreement with the ones $c_{\text{i,EDX}}$ computed using the built-in program for EDX included in the LYRA3 TESCAN SEM instrument as seen in table 4. The mass ratios computed with our code are in relatively good agreement with the ones computed with the EDX built-in program despite some discrepancies probably due to our choice of computation method: the built-in program uses a more precise empirical method that can take into account higher order fluorescence which is an important error source (0%–15%) [21] in the FPM considered in this paper. The uncertainties on $c_{\text{i,EDX}}$ origin from the measurement of the yield of each elements in the x-ray spectrum. For $c_{\text{i,th}}$, the uncertainty on the yield measurement must be summed in quadrature with the 10.3% uncertainty on the cross sections from the ‘NIST 164 database of cross sections for inner-shell ionization by electron’ [27] which explains why the uncertainties on the mass ratios computed by our code are higher than the ones given by the commercial EDX spectrometer.

### 3.3. Sensitivity study of the quantitative analysis related to the number of protons/x-rays

Since laser sources have inherent shot-to-shot fluctuations, both in energy and pointing stability, this affects the laser–matter interaction and, consequently, also the generation of secondary sources. Moreover, the focal spot’s Rayleigh length was about 10 μm [29], thereby fixing stringent alignment conditions when irradiating the 5 μm thick Cu target with the laser. Small deviations from the focal spot position (i.e. within tens of microns) modify the on-target intensity which induce large fluctuations in the proton and x-ray spectra. The small 2.5% root mean square (RMS) [31] fluctuations in the laser pulse energy are also partly responsible for this variation. In our calculations, we used the proton spectrum $f_p(E)$ and the number of incident x-rays $I_{\text{x}},i$ and $I_{\text{px}},i$ as obtained from the laser–matter interaction, averaged over 10 laser shots. However, the samples were probed with a single shot, producing secondary sources that have a high probability (68%) to be contained within the errorbars of the measured spectra. As mentioned in section 2.3, XRF will not induce K-line x-ray emission if all the elements constituting the sample have higher Z than the source. For instance, this is the case for the brass sample. In this case, only PIXE is responsible for this variation. In our calculations, we used the proton spectrum $f_p(E)$ and the number of incident x-rays $I_{\text{x}},i$ and $I_{\text{px}},i$ as obtained from the laser–matter interaction, averaged over 10 laser shots.

The table below compares the mass ratios computed with the built-in EDX code and the MATLAB® routine.

| Sample          | Element | $c_{\text{i,EDX}}$ (%) | $c_{\text{i,th}}$ (%) |
|-----------------|---------|------------------------|------------------------|
| Stainless steel | Ca      | 0.12 ± 0.01            | 0.19 ± 0.04            |
|                 | Cr      | 16.2 ± 0.5             | 18 ± 3                 |
|                 | Fe      | 57 ± 2                 | 57 ± 8                 |
|                 | Ni      | 7.4 ± 0.2              | 8 ± 1                  |
| Bronze          | Fe      | 4.6 ± 0.1              | 5.1 ± 0.7              |
|                 | Cu      | 75 ± 2                 | 64 ± 8                 |
| Brass           | Cu      | 63 ± 2                 | 53 ± 8                 |
|                 | Zn      | 20.4 ± 0.7             | 17 ± 3                 |

### Table 4. Comparison between the mass ratios computed with the built-in EDX program and our MATLAB® routine.
let the number of protons/x-rays obtained by the sources vary as shown in equation (6).

\[ Y_{i}^{th} = aY_{X,i} + bY_{p,i}. \] (6)

We reproduce the iteration procedure described in section 2.4 for values of \( a \) and \( b \) in increment of 0.05 to retrieve the mass ratios \( c_i \) corresponding to this modified source of protons and x-rays. To obtain a comparison basis, we then compute the relative RMS (root mean square relative error) of this new set of \( c_i \) with respect to the nominal ones presented in figure 4 for which \( a = b = 1 \). This procedure is presented in figure 5 for a stainless steel sample and indicates how the error on the sources affects the output RMS error for a given set of \( a \) and \( b \). Along the line \( a = b \) there is no deviation from the nominal values of \( c_i \) (obtained at \( a = b = 1 \)) since changing \( a \) and \( b \) by the same amount consists in multiplying the yield by a constant scaling factor. In the iterative process this scaling is then re-normalized when the normalization is performed on the simulated yields. For the worst case scenario, the case \( a = 1.25 \) and \( b = 0.85 \) (limit of uncertainty bounds), the RMS error is of about 16%, which means that an error of 25% on the x-ray and 15% on the proton spectrum yields an average error of 16% on the mass proportions for stainless steel. The mass proportions calculations are thus less sensitive than the sum of the individual errorbars of the sources.

3.4. Discussion about the depth probed by protons
The XPIF quantitative analysis is restricted by the maximum depth that can be probed in a material. This depends on the proton maximum energy as well as the type of material. For instance, with the 5 MeV maximum energy of our proton source, protons can potentially induce fluorescence up to 80 \( \mu \)m in stainless steel since their Bragg peak is located at this depth. However, the emitted x-ray photons have to travel back to the surface of the sample in order to be captured by the detector. These photons are strongly attenuated by the material along their paths to exit the sample. The transmission factor of about \( 1 \times 10^{-2} \) can be seen on figure 6(A) when a Fe K\( \alpha \) line at 6.4 keV is considered. Consequently, there must be enough protons to compensate this photon attenuation. To get an order of magnitude for the number of photons created per impinging proton at the corresponding depth \( R = \int_{E_0}^{E} \frac{d\Phi}{dE} \) for protons of energy \( E_0 \), we can use (1a) and compute (using the solution to the optimization problem for the stainless steel sample presented on figure 4) the number of x-rays generated by protons on a stainless steel sample. For 5 MeV protons, corresponding to a range of 80 \( \mu \)m, the number of detected photons per protons ranges in the order of \( 10^{-5} \) for the elements typically contained in stainless steel. The number of incident protons at 5 MeV (integrated number between 4.5 and 5 MeV for the solid angle subtended by the sample) for our source is in the order of \( 10^6 \) which yields a very low number of detected x-rays coming from this depth. Because of the low x-ray transmission factor, increasing the energy of the protons without accordingly increasing the number of protons might not produce new information about the sample with depth. Nevertheless, it is interesting to quantify the contribution to the photon yield produced by each proton energies at all depths since protons interact with electrons during the totality of their path in the material. Figures 6(B) and (C) respectively display the ratio of detected photons per impinging protons for different elements and the total number of...
Figure 6. (A) Proton range and corresponding transmission factor of the PIXE at different depths in a stainless steel sample. Even if protons can induce fluorescence up to a depth of 120 μm, the resulting photons cannot travel back to the surface due to the strong attenuation. (B) Ratio of the number of detected photons per impinging protons. (C) Total number of detected photons as a function of the source energy distribution.

detected photons according to the proton source (discretized in 10 bins with a width of 0.5 MeV, illustrated in figure 1(D)). We can conclude that even though higher energy protons (4–5 MeV) do not generate supplementary information in depth, they still have a higher contribution than low energy protons (0.5 MeV) during their travel. This can be explained by the energy dependence of the ionization cross section of K-shell electrons by protons $\sigma_{p,i}(E)$, which is approximately 1000 times greater at 5 MeV than at 0.5 MeV for the element Fe. Thus, even if the signal originating from the Bragg peak is too attenuated to be detected, higher energies still contribute to the analysis of materials for lower depths.

4. Conclusion

In this work, we showed that the laser-based XPIF technique allows for a quantitative analysis of material composition. As first step, we developed a MATLAB® routine to automatically generate a characteristic emission x-ray spectrum from the image of photons hits on a CCD x-ray camera, detect and assign the $K_{\alpha}$ and $K_{\beta}$ peaks with elements and compute the integrated yield $Y_i$ from the peaks. Through an iterative process, we then find the mass ratios $c_i$ which optimizes the fit between the experimental yields $Y_i$ and the simulated yields $Y_{i}^{th}$ computed with (1a) and (2a). Secondly, as a validation step, we tested three homogeneous metallic multi-element samples with our XPIF technique and with a reference commercial EDX spectrometer: stainless steel (made of Ca, Cr, Fe, Ni), bronze (Fe, Cu) and brass (Cu, Zn). The mass ratios obtained with XPIF are in agreement with the reference EDX data within the errorbars as shown on figure 4. We also validated the consistency of the FPM by testing the MATLAB® routine with electrons to reproduce the XRF mass ratios without the built-in software of the EDX spectrometer as demonstrated in table 2.

The presented XPIF method contains some limitations. For instance, our detector restricts the study of materials to elements of atomic number ($Z > 14$). This issue can be settled by an adequate detector choice in order to cover the desired energy range for materials of interest. Regarding the complexity of the spectra analysis, when probing samples composed of a large amount of various elements, such as minerals with an heterogeneous structure, emission lines can overlap or be unresolved in the spectra. In this case, the process of assigning each emission line to its corresponding element could be aided by machine learning classification [30]. Finally, the need for a 200 TW laser system is the most stringent constraint because of the infrastructure costs and size. Nevertheless, it is still cheaper and more compact than most conventional proton beam accelerators.

The major advantage of our technique is that it requires no previous knowledge of the sample’s composition compared to other empirical methods. Additionally, by combining both XRF and PIXE, the XPIF technique offers a higher yield than laser-based PIXE without x-rays. To improve the accuracy of the method, the proton energy spectrum must enable a high-repetition rate and smaller fluctuations to further enhance the x-ray and proton yields, along with the reduction of their associated uncertainties. A higher repetition rate allows for a cumulative analysis over multiple shots that would generate a greater number of x-ray photons. The total yield could be increased by a factor of 400 with an upgraded solid target positioning system compared to the current system [31, 32]. Efforts are currently being directed toward the realization of a 0.625 Hz (repetition rate) with 800 solid targets. With such a system, significantly higher particle fluxes will be generated, hence a better accuracy in the mass ratios.
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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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