

## CALCULATION OF THE DETECTOR-CONTRIBUTION TO ZIRCONIUM PEAKS IN EDXRF SPECTRA OBTAINED WITH A SI-DRIFT DETECTOR

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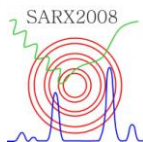
### ABSTRACT

Si-drift detectors may originate strong spurious peaks generated by the excitation of the built-in collimator. Peaks of these elements in the spectra may be attributed both to their presence in the object under analysis and to their presence in the ring, thus creating ambiguity in the interpretation and quantification of the results. Although an external collimator can be added to prevent photons to reach the ring, thus avoiding its excitation, this solution has several drawbacks. So, for most applications, the best approach is to allow this ring contribution to happen and estimate its value, so that the contribution from the object under analysis can be inferred. The intensities of Zr K-lines originated from a Zr ring, for instance, can be calculated taking into account the photoelectric absorption coefficients of Zr for each energy of the spectra above the respective absorption edge, the intensity of radiation, the probability of each line, and a geometric factor. The intensity profile of the radiation that reaches the ring can be taken directly from the spectrum, corrected for the detector efficiency and expurgated from escape and sum peaks. The geometric factor can be calculated by calibration with standard samples. This paper presents the attainment of these calibration constants and the estimation of the contribution of the collimator to the Zr peak, in a semi-portable EDXRF device. The X-Ray source was a ItalStructures W-tube, operated up to 60 kV. The measurements were made with a Ketek Si-drift detector with Zr collimator, with an upper measuring limit of around 29 keV. The effect of radiation above 29 keV was estimated from a) the background profile from 18 to 29 keV, and b) the estimated areas of K-peaks of elements which were detected through their L-peaks. The effect of the background was studied by using samples with no elements above Zr. The effect of excitation of Zr K-lines by measured characteristic lines was studied with samples containing Pd, Ag and Sn.

### INTRODUCTION

Si-drift detectors may originate strong spurious peaks generated by the excitation of the built-in collimator [1, 2]. Peaks of these elements — for instance Zr or Ag — in the spectra may be attributed both to their presence in the object under analysis and to their presence in the ring, thus creating ambiguity in the interpretation and quantification of the results. Although an external collimator can be added to prevent photons to reach the ring, thus avoiding its excitation [2], this solution has several drawbacks: a) the sample-detector distance has to be increased, b) the count-rate will decrease, c) the analysis spot will be mainly defined by this collimator, and d) the collimator itself will generate spurious peaks.

So, for most applications, the best approach is to allow this ring contribution to happen and estimate its value, so that the contribution from the object under analysis can be inferred [1]. Zr K-lines from the ring, for instance, will be excited by every photon with energy above the Zr-K absorption edge, and their intensity can be calculated taking into account the photoelectric absorption coefficients of Zr for each energy, the intensity of radiation, the probability of each line, and a geometric factor. The intensity profile of the radiation that reaches the ring can be taken directly from the spectrum, corrected for the detector efficiency and expurgated from escape and sum peaks. However, if the



detector was not configured to measure part of the spectra, this cannot be done, because every photon above the Zr-K absorption edge will excite the Zr ring.

In this case, instead of calculating directly the effect, one should try to establish a mathematical relationship between the known part of the spectra and the intensity of the Zr-ring. For one side, the background average intensity above the Zr-K absorption edge is a candidate as representative of the whole continuum profile above this absorption edge. For other side, L- or M-peaks may be used to estimate characteristic peaks which exist above the upper limit of the detector.

This paper presents the attainment of these relationships and the estimation of the contribution of the collimator to the Zr peak, in a semi-portable EDXRF device [2, 3].

## MATERIALS AND METHODS

The EDXRF spectrometer consists of an X-ray generator and an X-ray detector, and was developed at EPUSP. The generator is an Ital Structures W-tube, with voltage range from 22 to 60 kV and current from 0.12 to 1.5 mA. The detector is a Ketek AXAS Si-drift one, with an upper measuring limit of around 29 keV, with Peltier cooling, linked to a Ketek 4k-channel analog-digital converter. For the present measurements, a 1,3 mm-diameter Pb collimator was used in the incident beam, and the angle between the axis of the incident beam and the detector was 90°, both at 45° of the surface. The distance between sample and detector is 7 mm. Refrigerated water cooling was used in order to keep the detector case below 20°C, thus assuring a peak FWHM of around 150 eV. Most measurements were made at 55 kV, for 600 s, with an adequate current to ensure a FWHM of about 150 keV for the main peaks.

To establish the effect of the continuum above Zr K absorption edge on the intensity of Zr-K peaks, spectra of pure Si, Ti, Fe, Ni, Cu, W, Au and Pb were obtained at the standard configuration. To establish the effect of characteristic peaks above the absorption edge, pure Pd, pure Ag and a Sn-alloy were analysed. To check the validity of the developed model, spectra of standard alloys from BAS were obtained.

The areas of the Zr peaks were measured by the PyMCA software [4]. The areas of the background above Zr-K absorption edge were calculated from the background fitting curves obtained in the software, in the mode “linear polynomial” with order 3.

## RESULTS

Spectra for pure Si, Ti, Fe, Ni, Cu, Zr, Pd and Ag are shown in Figure 1. All of them present K-peaks of the constituent element and the spurious Zr K- and L-peaks. The average intensity of the background above the Zr-K absorption edge for these spectra is shown as function of the atomic number in Figure 2. The decrease of this intensity with Z allows a very good exponential fitting, with  $R^2 = 0.9879$ . The area of the spurious Zr-K $\alpha$  peaks also decreases with Z for the elements below Zr, as can be seen in Figure 3 (it should be remarked that the fitting of Zr-K $\alpha$  peaks required extreme care in the case of Ni and Cu, because of the partial overlapping of these peaks with Ni-K and Cu-K pile-up peaks). This behaviour also allows a very good exponential fitting, with  $R^2 = 0.993$ .

The exponential factors of the curves of background intensity and Zr peak areas versus Z present close exponential factors (-2.5755 and -2.3965, respectively), which suggests that a reasonable relationship can be established directly between these values with a lower exponential factor. This is confirmed in Figure 4, which shows a good exponential fitting:

$$A_{bs} = 170.0 B^{0.8175} \quad (\text{equation I})$$

where  $A_{bs}$  is the intensity of the Zr-K $\alpha$  peak (“b” accounts for “background” and “s” accounts for “spurious”) and B is the average background intensity.

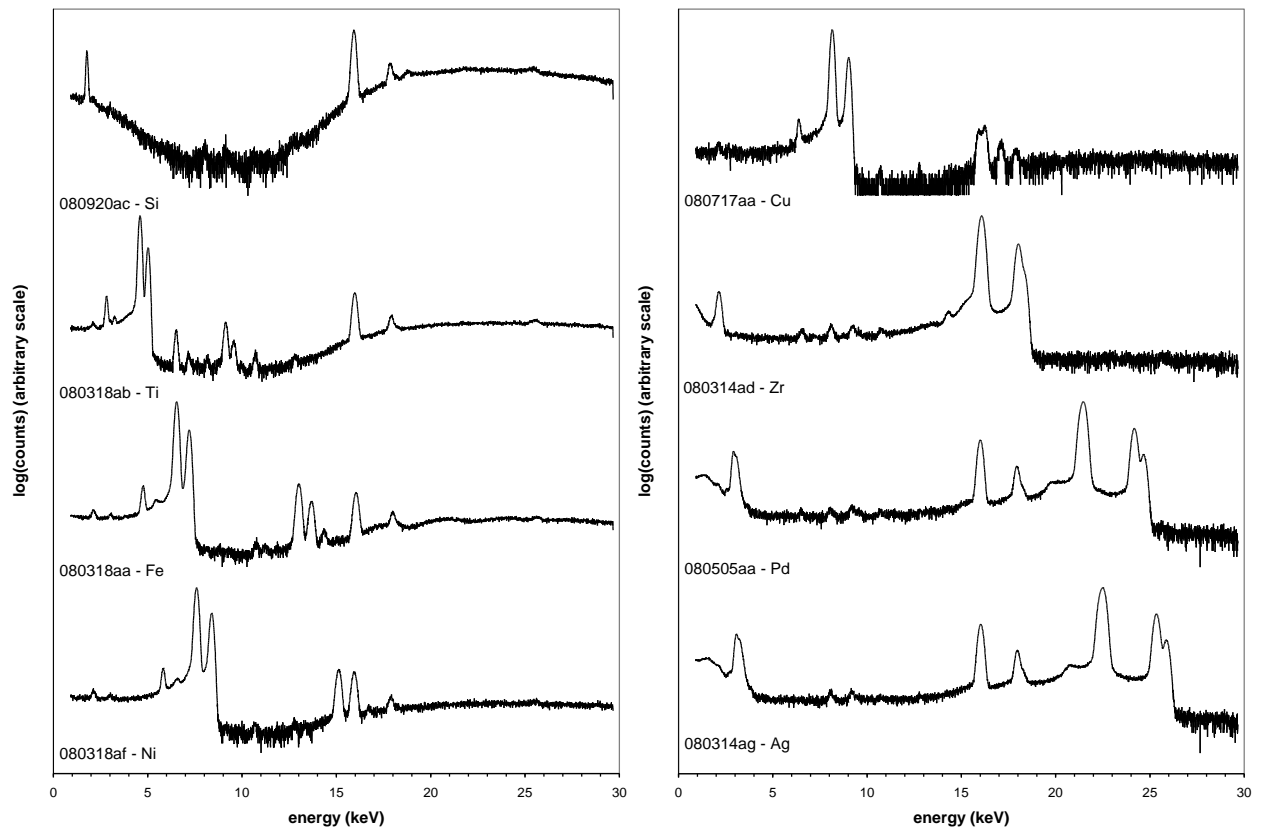


Figure 1 – Spectra of pure Si, Ti, Fe, Ni, Cu, Zr, Pd and Ag. Zr-K peaks are at 16.62 and 18.62 keV.

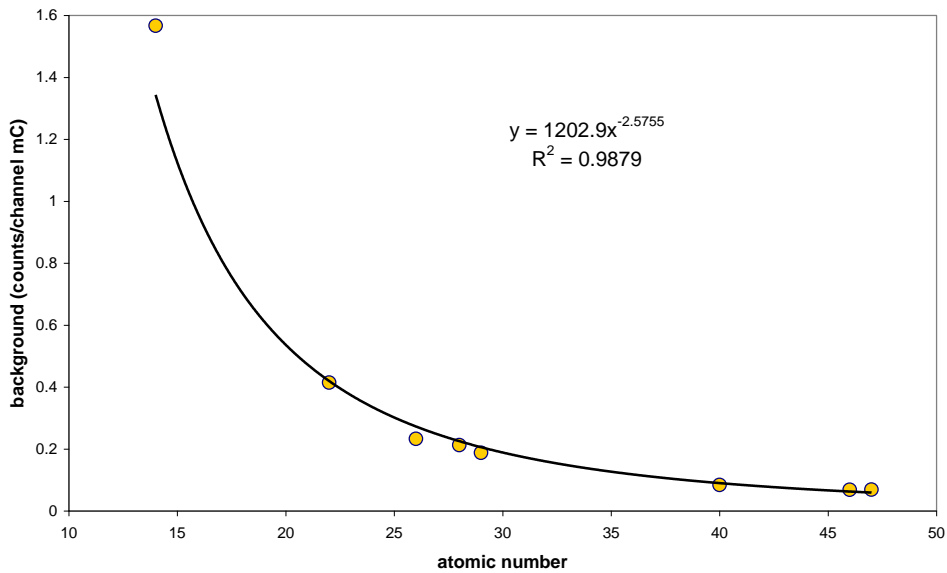


Figure 2 – Average intensity of the background above the Zr K-absorption edge versus Z

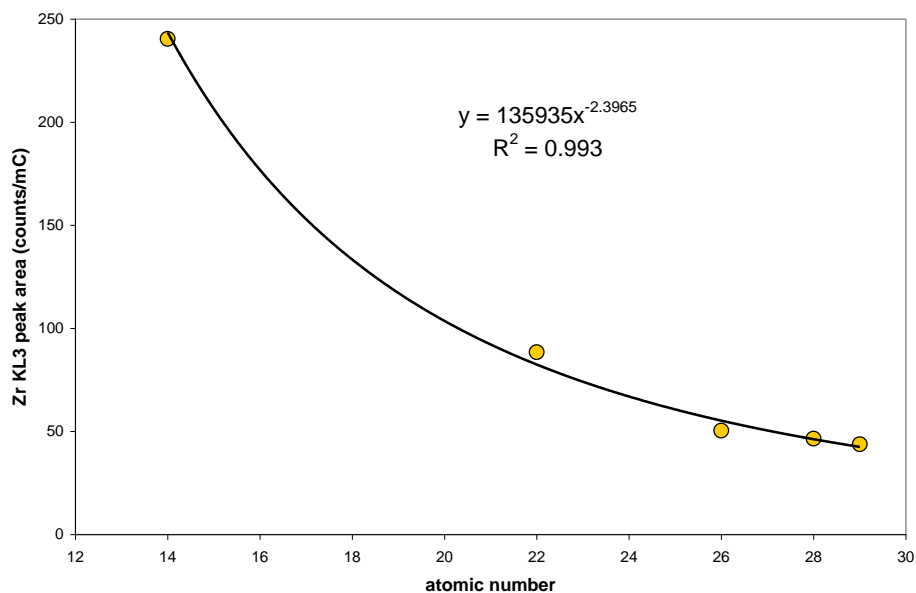


Figure 3 – Area of the spurious Zr-K $\alpha$  peaks for the spectra versus Z

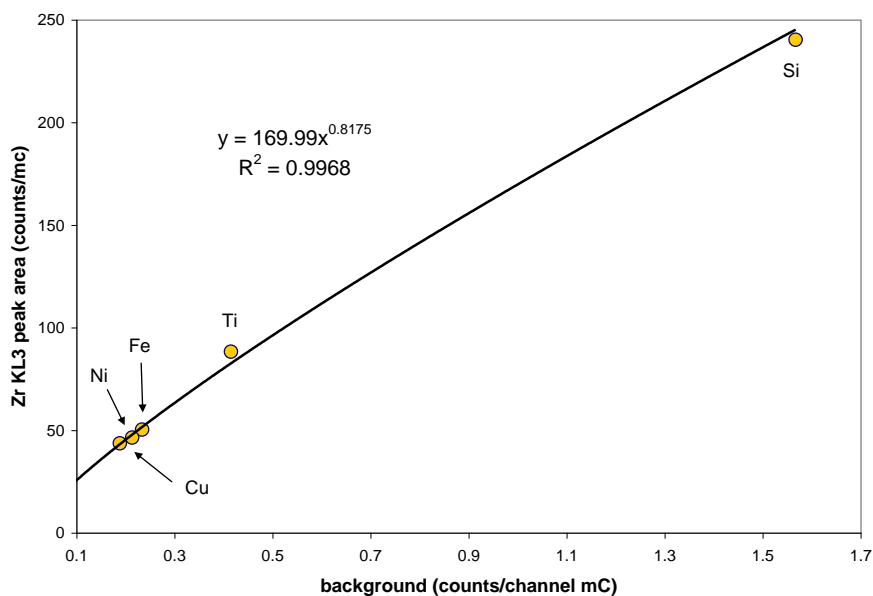


Figure 4 – Area of the spurious Zr-K $\alpha$  peaks as function of the average intensity of the background above the Zr K-absorption edge

Such a good fitting, however, could not be established for heavier elements. If they have characteristic peaks above the Zr-K absorption edge (as Pd and Ag in Figure 1, for instance), the spurious Zr-K peaks are much more intense than predicted by equation 1. The effect of these characteristic peaks can be estimated taking into account the photoelectric absorption coefficients of Zr for each energy, the intensity of radiation and the probability of each line, giving rise to a theoretical Zr-K $\alpha$  peak area,  $A_{ts}$ , in an arbitrary scale (“t” accounts for “theoretical” and “s” for “spurious”). To obtain an absolute theoretical value, however, the geometry of the spectrometer and specifically that of the detector ring should be considered. Instead of that, we obtained calibration constants. For this, the theoretical effect was calculated without any geometrical considerations, assuming an arbitrary intensity scale. These

values were compared to the difference between the experimental Zr-K $\alpha$  peak-areas and the background estimated contribution.

Table 1 shows the areas of the characteristic peaks of Pd and Ag, the theoretical areas of the spurious Zr-K $\alpha$  peaks ( $A_{ts}$ ) which would be generated by those characteristic peaks (in an arbitrary scale), the experimental Zr-K $\alpha$  peak area ( $A_{exp}$ ), the average background intensity and the estimated contribution of the background from equation 1. From the difference  $A_{ep}$  (“ep” accounts for “effect of peaks”), given by  $A_{ep} = A_{exp} - A_{bs}$ , a calibration constant ( $K_g = A_{ts} / A_{ep}$ ) for the effect of the characteristic peaks is obtained as a linear function of the wavelength  $\lambda$  of the exciting characteristic peak (a geometrical average of the wavelengths of K $\alpha$  and K $\beta$  was taken for this):

$$K_g(\lambda) = -3.636 + 8.526 \lambda \quad (\text{equation 2})$$

where  $\lambda$  is expressed in Angstrom.

As shown in Figure 5, a good  $R^2$  was obtained for this fitting: 0.9997.

Table 1 – Calculation of the constant  $K_g$ .

Areas are given in counts/mC. The average background intensity is given in counts/(channel mC).

	KL3 area	KM3 area	$A_{ts}$	$A_{exp}$	B	$A_{bs}$	$A_{ep}$	$K_g$
Pd	22200	433	1562	1309	0.275	59	1249	1.25
Ag	25067	490	1563	1593	0.277	60	1533	1.02
Sn	4093	705	180	525	0.713	129	396	0.45

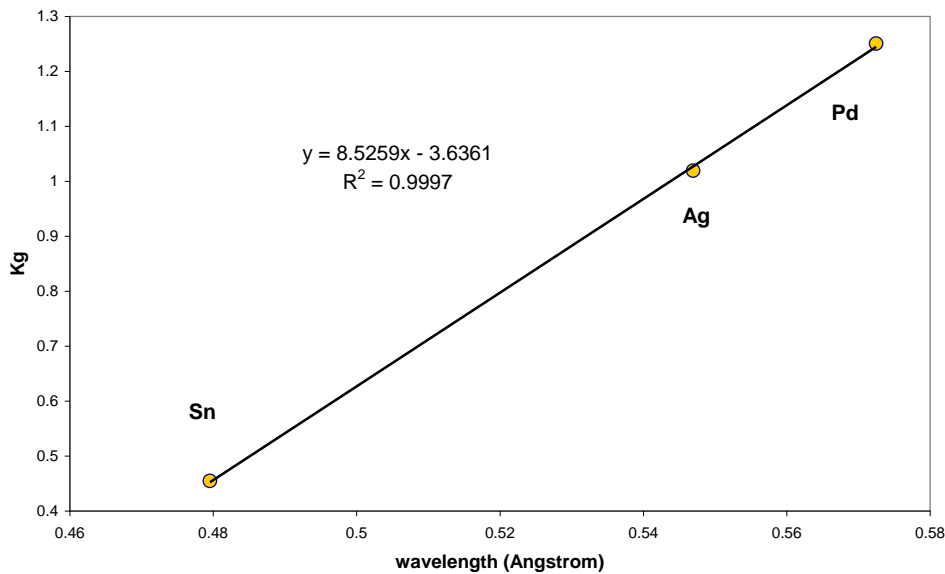


Figure 5 –  $K_g$  as function of the average wavelength of the exciting radiation

Therefore, for a generic sample, the estimated total area  $A_{es}$  of the spurious Zr-K $\alpha$  peak is given by:

$$A_{es} = A_{bs} + \sum ( A_{ep}(i) / K_g(\lambda) ) \quad (\text{equation 3})$$

where  $\sum ( A_{ep}(i) / K_g(\lambda) )$  is the sum of the calculated effects  $A_{ps}(i)$  for each element  $i$ , corrected by the calibration constant. If the characteristic peaks of the sample are above the measuring energy limit of the detector, their intensities are estimated from the intensities of L- or M-peaks of the element present

in the spectrum. Therefore, the part of a Zr-K $\alpha$  experimental peak that can be attributed to the true presence of Zr in the sample,  $A_{\text{true}}$ , can be estimated by:

$$A_{\text{true}} = A_{\text{exp}} - A_{\text{ts}} \quad (\text{equation 4})$$

This model was applied to Zr-free copper-alloy standard samples, through a routine in the Fundamental Parameters software developed by our group. Figure 6 shows the spectra of these samples, Table 2 shows their nominal compositions and Table 3 shows the areas of K-peaks for S and Sb (the only peaks above the Zr-K absorption edge observed in these spectra), the estimated effect of them on the Zr-K $\alpha$  spurious peak ( $A_{\text{ep}}$ ), the corrected values ( $A_{\text{ep}}/K_g$ ) and its sum, the background and estimated effect of background (B and  $A_{\text{bs}}$ , respectively), the total estimated intensity ( $A_{\text{es}}$ ) and the experimental intensity ( $A_{\text{exp}}$ ). One can see that a very good agreement between  $A_{\text{es}}$  and  $A_{\text{exp}}$  was obtained.

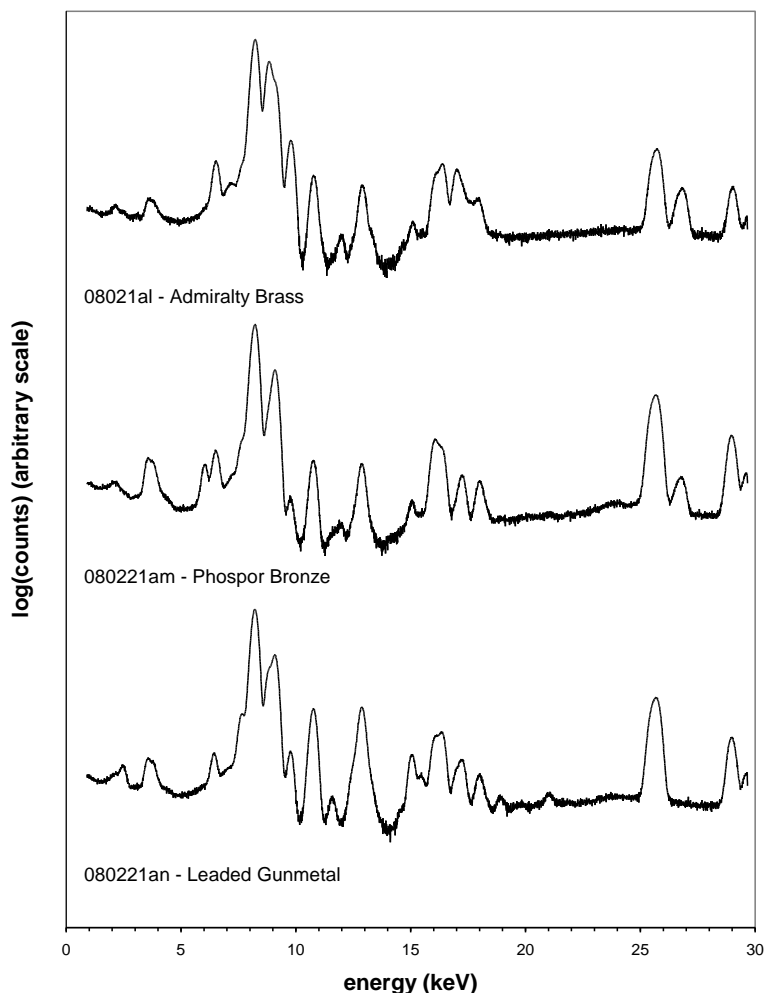


Figure 6 – Spectra of three standard copper-alloy samples from BAS (Bureau of Analysed Samples, UK). Sn-K peaks are at 25.27 and 28.47 keV. Sb-K peaks are at 26.36 and 29.73 keV. Zr-K spurious peaks are partially overlapped by pile-up peaks.

Table 2 – Composition of three standard copper-alloy samples from BAS (Bureau of Analysed Samples, UK), in mass fractions

	1 - Admiralty Brass	2 - Phosphor Bronze	3 - Leaded Gunmetal
Mn	0.00019	0.00419	0.000005
Fe	0.00354	0	0.00003
Ni	0.00168	0.00536	0.001
Cu	0.7436	0.8654	0.8391
Zn	0.2213	0.0109	0.0475
As	0.00168	0.00106	0.00001
Sn	0.0163	0.0947	0.0491
Sb	0.00356	0.0033	0.00002
Pb	0.00575	0.0079	0.0501

Table 3 – Estimation of the spurious Zr-K peak area for the three BAS standard samples (see Table 2). Areas are given in counts/mC. The average background intensity is given in counts/(channel mC).

sample / peak	KL3 area	KM3 area	$A_{ep}$	$\lambda$ (Å)	$K_g$	$A_{ep}/K_g$	sum	B	$A_{bs}$	$A_{es}$	$A_{exp}$	
1	Sn	241.92	49.97	10.65	0.393	0.45	24	30	0.17	39	69	71
	Sb	45.90	9.54	1.806	0.376	0.28	6					
2	Sn	1443.59	298.97	63.54	0.393	0.45	141	147	0.24	53	200	196
	Sb	39.62	8.26	1.56	0.376	0.28	6					
3	Sn	720.51	149.10	31.71	0.393	0.45	70	70	0.22	50	120	127
	Sb	0.58	0.12	0.023	0.376	0.28	0.08					

One should remark, however, that all this method relies on equation 1, based on samples with  $Z < 40$ , which do not present characteristic peaks above the Zr-K absorption edge. For heavier elements which also do not present these peaks (up to the maximum energy of the incident beam), however, the equation was observed not to be valid. Figure 7 shows the plot of the areas of the Zr-K $\alpha$  peaks versus the background intensity for pure W, Au and Pb. Figure 8 shows their spectra. One observes that not only the background intensity does not follow the monotonous behaviour shown in Figure 2, but also that it cannot be used to predict the area of the spurious Zr peak. For samples with high contents of these elements, therefore, the whole spectrum should be necessary for this prediction.

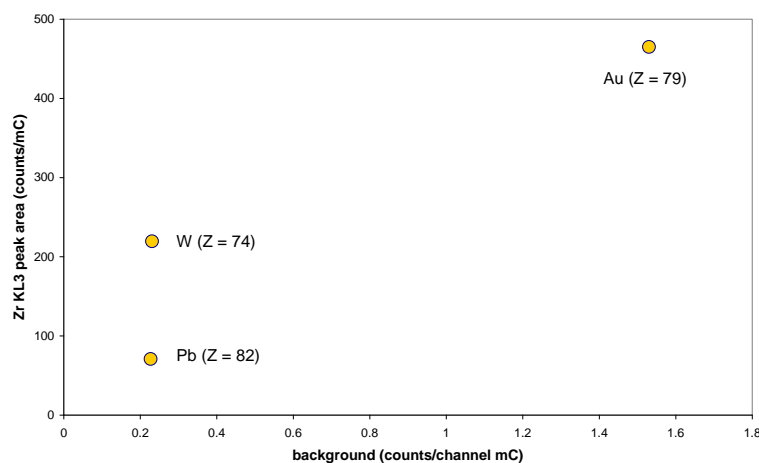


Figure 7 – Area of the spurious Zr-K $\alpha$  peaks as function of the average intensity of the background above the Zr K-absorption edge

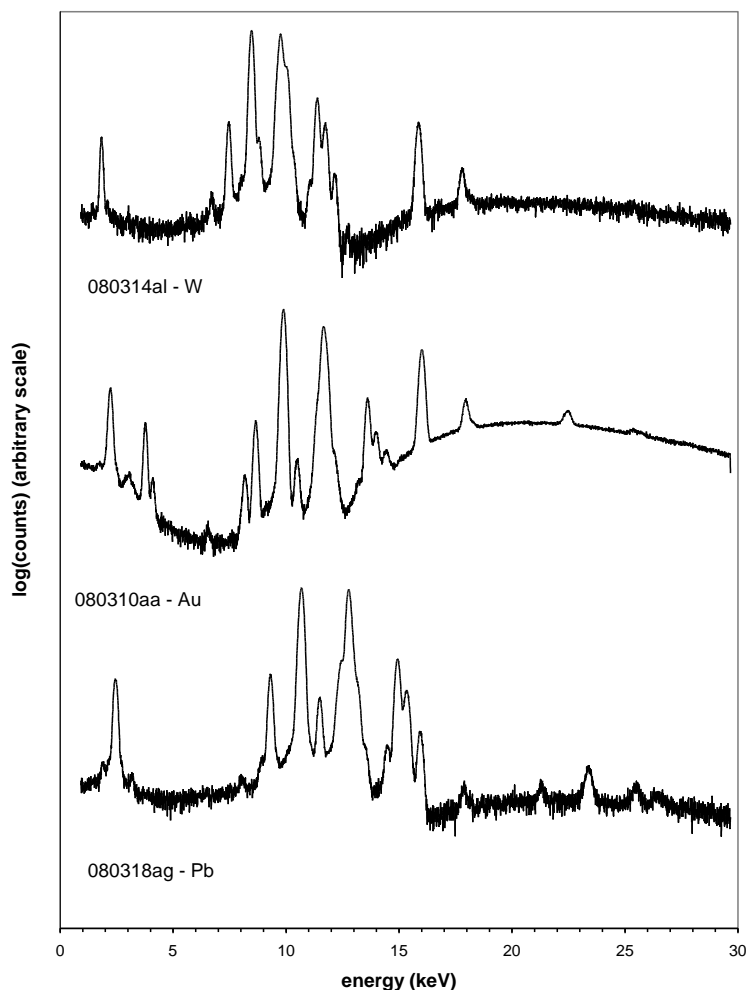


Figure 8 – Spectra of pure W, Au and Pb. Zr-K peaks are at 16.62 and 18.62 keV. Pile-up peaks are observed above Zr-K spurious peaks.

## CONCLUSION

Even if a complete spectrum is not available, the intensity of the spurious Zr-K $\alpha$  peaks can be estimated from the intensity of the background and of characteristic peaks above the Zr-K absorption edge, so that the presence and the true content of Zr from the sample can be estimated. The model was successful for Zr-free copper-alloy standard samples. However, it should not give precise results for alloys containing high contents of elements above W.

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