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Angle-resolved Electron Probe Microanalysis revisited:

J. Cazaux

GRESPI/Matériaux Fonctionnels UFR Sciences Exactes et Naturelles
B.P 1039, 51687 REIMS CEDEX 2, FRANCE

Abstract.

In Electron Probe Microanalysis (EPMA), the general strategy of characterizing specimens with their depth-dependent composition consists of changing the incident beam energy, E^0 , in order to change the effective thickness of the electron-irradiated volume. Initiated by two pioneering works an alternative way consists of changing the take-off angle of the measured characteristic x-ray line intensities but keeping unchanged the excitation conditions and the detector's position. In continuity to these previous investigations the present contribution suggests several improvements and applications for Angle-Resolved Electron Probe Microanalysis (AR-EPMA). In particular optimized angular conditions are defined and a new sample set-up is proposed. A simple model of $\Phi(z)$ function is also used to simulate various angular profiles relative to a variety of situations including inhomogeneous in-depth concentration profiles and multi-stratified samples, etc. Comparisons to published data are also performed when available and the relative advantages of AR-EPMA to conventional EPMA are discussed. The suggested device may be implemented into dedicated electron microprobes but its implementation into a SEM (+ EDS equipment) seems the most promising for rapid and automatic acquisitions of angular profiles at selected points of a sample. The same device may also be used for other beam techniques such as Auger Electron Spectroscopy: AR-AES.

1° Introduction

Since the pioneering work of Castaing in 1951, considerable efforts have been made to improve the performance and the fields of application of Electron Probe Microanalysis (EPMA) [1][2]. For 60 years, this now mature technique has been conventionally applied to bulk specimens to obtain elementary chemical analyses of micro volumes of the order of $1\text{ }\mu\text{m}^3$ [3] and, besides many practical applications, the efforts of the scientific community were and are mainly focused towards two directions: the improvement of the quantification procedures of homogeneous samples and the characterization, in a non-destructive manner, of samples that have a depth-dependent composition. For reaching these goals, the basic experimental procedures remain nearly unchanged with an exception: the change of the incident beam energy, E° , in order to change the effective thickness of the electron-irradiated volume and, then, the thickness from which are issued the characteristic x-ray lines being detected. The decrease of E° improves the surface sensitivity of the technique and the use of variable beam energies allows one to obtain z-concentration profiles: see ref. [4] from Pouchou and Pichoir and [5][6][7] for more recent reviews.

For the increase of the surface sensitivity as well as for depth-profiling purposes, an alternative approach consists of changing the take-off angle, θ , of the detected characteristic x-ray line intensities, $I(\theta)$. This changes the effective information depth of the signals by the change of their attenuation into the specimen as expressed by $\mu z \text{ cosec } \theta$ (μ : linear absorption coefficient). A similar strategy has been and is frequently for depth profiling of the few atomic layers composing a surface in angle-resolved X-ray photoelectron spectroscopy (AR-XPS) [8] but the corresponding potentialities of AR-EPMA have been very scarcely explored. In fact only two papers have been devoted to this topic: that of Gennai et al., 1971, who used a ‘variable take-off angle method’ to measure the absorption factor, $f(\chi)$, in a dedicated electron microprobe, [9] and ref. incl., and that of Völkerer et al., 1998, who rotated a tilted sample round 180° in a Scanning Electron Microscope (SEM) to characterize some overlayers on homogeneous substrates [10]. The key point of these two approaches is that the characteristic x-ray line intensities, $I(\theta)$, are collected at variable take-off angles θ but keeping unchanged the excitation conditions and the detector’s position. The present contribution is in continuity to these two pioneering works.

In Section 2 simple geometrical considerations on a very schematic experimental arrangement permit to define the best angle of tilt to explore the largest θ -range as possible. Next, the angular intensity changes are evaluated in Section 3 for a variety of situations including

comparisons to previously published data. Then the present investigation concerns the effect of the absorption factor, $f(\chi)$, of homogeneous samples as well as the intensity changes of the substrate signals when this substrate is coated with overlayers of different thickness and composition but this investigation also concerns the cases of inhomogeneous in-depth distributions and of stratified samples, etc. Finally, Section 4, an improved experimental arrangement is suggested along with a discussion of the performance and applications of AR-EPMA with respect to conventional EPMA and to other analytical techniques.

2° Optimization of the investigated angular range.

In AR-XPS, a progressive tilt of the sample changes the take-off angle of the characteristic signals being collected. The correlated effects of such a tilt on the incident x-rays on the investigated surface layer may be easily taken into account [8]. Quite different is the situation of EPMA where such a sample tilt effectively changes the take-off angle of the detected characteristic signals, but simultaneously changes the distribution of ionization with depth. Gennai et al.[9] and on one hand, Völkerer et al.[10] have overcome this difficulty by setting the inclined sample on a rotating sample holder with a rotation axis co-axial to the incident beam: see Fig. 1a. Then, when the rotation angle ω is changed, the normal to the sample surface, ON, rotates around the incident beam. This leads to a change of the take-off angle θ , but keeps constant the excitation conditions- incident beam energy and angle i .

The equation relating θ to ω is a function of angle i -incident angle corresponding to the tilt of the sample- and of angle d - angle between the incident beam and the direction of the collected signals-. This equation is given in Eq. 1 in ref. [9] but this equation simplifies when the optimum angular conditions, the maximum angular range for θ , are satisfied. From Fig 1a it appears that the incident angle, i , may be made equal to d or to $90^\circ - d$. When the condition of $i=d$ is satisfied, the relationship between the rotation angle ω and the take off angle θ may be easily deduced from elementary geometrical considerations (See Fig.1b). It respects the following:

$$\sin \theta = 1 - (1 - \cos \omega) \sin^2 d \quad (1)$$

When the choice is $i=90^\circ-d$, the relationship between ω and θ is:

$$\cos \theta = 1 - (1 - \cos \omega) \sin^2 d \quad (1')$$

Fig. 1c shows the results of some numerical applications of Eqs.1 and 1'. When the constraint of an angle d between the incident beam and detector direction is greater than 45° , the full angular range of θ , from 0° to 90° , may be explored automatically from the choice of $i=d$.

When the angle d is less than 45° the choice of $i=90^\circ-d$ also permits one to obtain automatic θ -angle profiles in the interval of $0^\circ < \theta < 2d$.

All the other choices, $i \neq d$ and $i \neq 90^\circ-d$, lead to a reduction of the θ -angular range that may be explored. This is the case for the geometry used by Gennai et al., where the angular interval was $10^\circ \leq \theta \leq 40^\circ$; this is also the case for the geometry used by Völkerer et al, where the angular interval was $15^\circ \leq \theta \leq 50^\circ$.

For all the geometries, the important point is that excitation parameters - incident beam energy and intensity - remaining constant, the $\Phi(z)$ function is unchanged during the set of experiments. As shown in fig. 1a and initiated by Gennai et al. it is then possible to use a stepped motor for the ' ω -angle rotation' in order to record angular profiles. The corresponding device to be inserted into any kind of electron microprobe or of SEM (equipped with an EDS attachment) is detailed in Section 4.

3° Examples of simulated angular profiles.

3°1. Initial hypotheses. The goal of the present section is not to develop a theory or to suggest a new procedure for quantification in EPMA at an oblique incidence. It is just an over-simplified attempt to discover the main features that may be expected from the use of AR-EPMA. For this limited goal, a simplified model of the in-depth ionization function is used, $\Phi(z)$, where $\Phi(z) dz$ is the ratio of the number of ionizations (or characteristic intensity) that are issued from a thin layer that is embedded in a substrate relative to those that are issued from an unsupported layer of thickness dz and of the same composition and which is investigated under the same experimental conditions. The present choice of $\Phi(z)$ corresponds to a normal incidence while the optimized operating mode, $i=d$, is specific to each experimental arrangement and a better choice for $\Phi(z)$ would need to consider a too large variety of incident situations. Qualitatively the main effect of a sample tilt on the excitation conditions is a compression of the $\Phi(z)$ function towards the surface decreasing then the absorption effects similarly to the decrease of the incident beam energy. Then the present calculations at 15 keV and normal incidence nearly correspond to increasing beam energies when the sample tilt is increased. It also be kept in mind that the goal of present calculations is to evaluate the trends of the functions $f(\chi)$ and of the K ratios when θ is varied. The function $\Phi(z)$ appears in the numerator and in the denominator of fractions defining $f(\chi)$ and K -see below- so that the errors made on $\Phi(z)$ partly compensate each others: a fact also pointed out by Völkerer et al.[10].

Further, according to the arguments developed by Pingitore et al. [11], we prefer to use equations that involve the atomic densities, N_A , N_B , and atomic concentrations C_A , C_B , C_C , etc., of the elemental components of the sample, A, B, C, etc., instead of the widespread use of mass densities and mass fractions. Then, for x-ray photons of energy $h\nu$, the linear absorption coefficient, μ , is derived from the corresponding photo-absorption cross-sections, Q_A^x , Q_B^x , Q_C^x .

$$\mu = N_A Q_A^x + N_B Q_B^x + N_C Q_C^x + \dots \quad (2)$$

The starting equation that expresses the detected intensity for a pure element A is given by:

$$I(A_\infty) = F \int_0^\infty \Phi(z) \exp(-\mu z \csc \theta) dz \quad (3)$$

while the absorption factor, $f(\chi)$ is:

$$f(\chi) = \int_0^\infty \Phi(z) \exp(-\mu z \csc \theta) dz / \int_0^\infty \Phi(z) dz \quad (4)$$

The numerical evaluations below of μ result from the use of compilations of photo-absorption cross sections [12][13], which are illustrated in Fig 2 for the main elements of interest here, namely Mg, Al and Si.

3°2. Homogeneous samples. The present choice of the $\Phi(z)$ function is limited to the $K\alpha$ line of Al and to those of the neighboring elements, Mg and Si, and the Gaussian model of Packwood and Brown [14] is chosen because of its simplicity. As shown in Fig. 3a, this model fits very well the experimental results that Castaing & Descamps [15] obtained at $E^\circ=15$ keV by using the tracer method on pure Al at normal incidence. Its use is extended here to Mg and Si at the same beam energy and at the same oblique incidence. In the same Fig. 3a the influence of a change of the take-off angle, θ , on $\Phi(z) \exp(-\mu z \csc \theta)$ is also shown from the use of tabulated values for Q_{Al}^x (Al $K\alpha$) [12; 13]. Due to the low value of μ for Al $K\alpha$ radiations into Al, $\mu=0.12 \mu\text{m}^{-1}$, one may observe that the self-absorption effect is not very important, except for take-off angles below 15° . As suggested in Fig. 3b, the situation is significantly different for Al $K\alpha$ photons that propagate into a postulated Al-Mg alloy (C. at.=50% each) because of their significant absorption by Mg (μ is approximately $1.03 \mu\text{m}^{-1}$ for Al $K\alpha$ absorption by pure Mg). The results are shown in Fig. 4 where the emerging x-ray intensity, $I(\text{Al}_{50\%})$ has been evaluated from:

$$I(\text{Al}_{50\%}) = F \int_0^\infty C_{Al} \Phi(z) \exp(-\mu z \csc \theta) dz \quad (5)$$

Instead of performing algebraic integrations, the integrals of Eqs 3, 4 and 5 are better numerically performed from the discrete sum, $\sum$, of the elementary contributions of adjacent thickness layers, $z_i \pm \Delta z_i$ with $\pm \Delta z_i = \pm 0.05 \mu\text{m}$. These sums enable one to obtain the evolution of the absorption factor $f(\chi)$ as a function of the take-off angle θ . Fig 4a shows the results obtained for pure Al and for a postulated Al-Mg alloy (C=50% for each) with, in addition, the experimental results obtained at 30 keV by Gennai et al. for Fe K_α photons in pure Fe and in a Fe-Al_{24wt%} alloy. This figure shows the increased influence of self-absorption effects by pure Al for take-off angles below 30° while the strong absorption effects of Mg atoms for Al K_α photons lead to a decrease in $f(\chi)$ for take-off angles below 60° combined with an asymptotic value, at normal emergence, that is significantly less than 100%. The self absorption effects are less for Fe K_α into pure Fe, $\mu = 0.0436 \mu\text{m}^{-1}$, and into a Fe-Al_{24wt%}, $\mu = 0.046 \mu\text{m}^{-1}$, and the decrease of $f(\chi)$ is only significant for $\theta \leq 10^\circ$. With a self absorption coefficient $\mu \sim 1.7 \mu\text{m}^{-1}$ the measurement of $f(\chi)$ for the Fe L_α into pure Fe would lead to a significantly different behavior with a very low value for $\theta = 90^\circ$ and a rapid decrease with θ .

By following the same mathematical procedure, it is also possible to evaluate the K ratio between the characteristic intensity that is issued from a given sample and the characteristic intensity that is issued from a pure elemental standard. Some results are shown in Fig. 4b. They concern the above postulated Al-Mg alloy (C=50% each) for the Al K_α line, as well as for Mg K_α lines where, for the sake of simplicity, the $\Phi(z)$ function for Mg K photons absorbed by this alloy should be similar to that for Al K photons absorbed by the same alloy and by pure Al. For an evaluation of the corresponding K ratio, $K_{\text{MgK}}(\text{Mg}_{50\% \text{ at}; \text{Al}_{50\% \text{ at}}})$, the unique changes are the numerical values of the absorption coefficients, $\mu_{\text{MgK}}(\text{pure Mg}) \sim 0.086 \mu\text{m}^{-1}$ and $\mu_{\text{MgK}}(\text{pure Al}) \sim 0.17 \mu\text{m}^{-1}$. Here again the main result is the large absorption of Al K_α photons by Mg atoms, leading to a K ratio (a measure of the apparent concentration), $K_{\text{AlK}}(\text{Mg}_{50\% \text{ at}; \text{Al}_{50\% \text{ at}}})$, which is significantly below 50% at normal emergence and is decreasing rapidly with the decrease of the take-off angle. For the opposite reasons, the case of the Al-Be alloy, (Al_{90% at}; Be_{10% at}), is interesting because of the very low numerical value of the absorption coefficients, $\mu_{\text{AlK}}(\text{pure Be})$, $\sim 0.016 \mu\text{m}^{-1}$. When there are Be atoms on the sites of some initial Al atoms, the situation is similar to that of porous samples or samples that contain atomic vacancies. The very low value of μ explains a K ratio that is greater than 90%.

3° 3 Thin foils on bulk substrates.

The next step consists in investigating thin foils on homogeneous substrates. This type of investigation has been performed by Völkerer et al. to illustrate a new technique for

standardless analysis called EPMA-TWIX [10]. With an incident angle of $i \sim 20^\circ$ for a detector angle of $d = 55^\circ$, their operating conditions were not optimized so that the take-off angle was successively equals to $\theta = 15^\circ$ and to $\theta = 55^\circ$ when they performed two measurements by a horizontal rotation ω of 180° . The ratio of the detected intensities was called K_{twix} and it corresponds to $I(55^\circ)/I(15^\circ)$. Table I shows the experimental values of K_{twix} then obtained at $E^\circ = 20$ keV for the Si K_α line issued from a pure silicon substrate. In the same table the results of present calculations for K_{twix} are also shown with in addition, $K(15^\circ)$ and $K(55^\circ)$. For such calculations the absorption coefficients are the same as in [10] and the $\Phi(z)$ function for Si K_α at 20 keV and $i = 20^\circ$ is postulated to be similar to that shown in Fig. 3a at 15 keV and $i = 0^\circ$: the oblique incidence partly compensating the larger beam energy. Despite such a crude approximation the fairly good agreement between experiments and calculations is not surprising because a K ratio involves the same $\Phi(z)$ function in the numerator and in the denominator of the corresponding fraction so the errors made on $\Phi(z)$ partly compensate each others: an argument also given by Völkerer et al. to justify their standardless method.

The most important point is that a 3 nm-thick Au layer or a 8.5 nm-thick Al layer leads to measurable changes in the Si-substrate intensities even under non-optimized operating conditions. Being governed by a value of μt less than 0.01 the same measurable changes may be expected for other coatings on Si such as a SiO_2 layer of thickness at about 30 nm or a carbon layer of thickness at about 100 nm. The same results may be expected for other substrates such as aluminum oxide layers on Al substrates, etc.

The investigations of the present section are focused on the information carried by the attenuation of the x-ray signals issued from the substrate but the simultaneous acquisition of signal issued from the overlayer also provides very useful information for its thickness determination. As illustrated in the section below, Figs 5a, the K ratio of characteristic signals issued from a thin overlayer is nearly independent from the take-off angle θ except at low emerging angles where it increases. Its value as well as its intensity relative to that the substrate increases when the beam energy E° is lowered, as the result of an increased confinement of incident electrons into the surface layer.

3°4. Stratified samples.

The stratified samples now considered are composed of two layers, each 0.5 μm thick, on a substrate. Pure Mg, Al and Si are successively involved in each of the three regions in such a way that all of the possible combinations are considered (e.g., Al/Mg/Si, Si/Al/Mg, Al/Si/Mg, etc.). For each situation, the evaluated K ratio corresponds to the ratio of characteristic

intensities that are being determined for the sample and the pure element standard that has the same take-off angle. In Figure 5a, the change in the corresponding K ratios as a function of θ is illustrated for the characteristic signals that are issued from the top layer. Postulating a similar $\Phi(z)$ function for the three elements, the observed evolutions are very similar and they differ only by the numerical value of their self-absorption coefficients, μ . The observed increase in K with the decrease in θ is easily understood. It corresponds mainly to the decrease in $\Phi(z) \exp(-\mu z \csc \theta)$ - Fig. 3a- leading to a decrease in $f(\chi)$ - Fig. 4a - of the pure standards.

As seen in Fig. 4b, the evolution of the K ratios for the characteristic x-rays that are issued from the substrate is quite different. They all decrease with θ because of the increased attenuations of characteristic x-rays across the overlayers. Nevertheless, these attenuations depend strongly on the energy of the characteristic x-lines relative to the absorption edges of the two other elements. From Fig. 2, it is easy to explain the observed lower attenuation of the MgK_α intensities and the greater attenuation of the SiK_α intensities, while the AlK_α intensities are attenuated mainly by the Mg overlayer and significantly less by the Si overlayer. The same explanations are easily transposed to the K_α intensities that issue from the intermediate layer when it is sandwiched between an overlayer and a substrate of different compositions. See Fig 6.

An important point to note is that Figures 5 and 6 differ from all of the others. Then, when the angular profiles relative to pure elemental standards have been pre-acquired, a rapid identification of the structure of a given layered sample is possible from the parallel acquisition of only a single series of angular profiles of the analyzed sample. The fundamental aspect is the possibility of extracting useful information from the attenuation of a given characteristic line by the other components of the sample, instead of limiting the effects of absorption to the need of a correction procedure.

3°5. Variable z-concentration profiles.

The above examples concern stratified materials with abrupt interfaces where only measurements at a few selected angles are needed. An interesting situation occurs when the in-depth concentration of the species continuously changes. When the variable beam energy method is used, such a situation requires a large number of experiments at energies E° very close to each others. In contrast the automatic acquisition of series of angular profiles permits a rapid identification of such a distribution. To illustrate this point, one consider the case of a hypothetical binary alloy, AlMg , with an in-depth concentration gradient of Mg having a

Gaussian profile (See Fig 7a). For such an alloy, the K ratio for AlK_α is very sensitive to an in-depth change in the Mg concentration because of the large absorption of this x-ray line by the Mg atoms. In contrast, with a value of μ , $\mu_{\text{MgK}}(\text{Al})$, that is very similar to $\mu_{\text{MgK}}(\text{Mg})$ the absorption effects for MgK_α by the Al atoms are rather weak. This explains, therefore, the difference in angular evolution of the two K ratio that appears in Fig. 7b. There is a significant decrease for $K(\text{Al})$ with θ and a nearly constant evolution for $K(\text{Mg})$ but there is also the significant difference between the decreases for $K(\text{Al})$ with θ for the alloy with a Gaussian concentration profile and that of a constant in-depth concentration. This last point is also illustrated in Figure 7b where are also shown the changes of the two K ratios, $K(\text{Al})$ and $K(\text{Mg})$, for a $\text{Al}_{72\%}$ at $\text{Mg}_{28\%}$ at homogeneous alloy.

3°6. Influence of the incident beam energy E° and other experimental considerations.

Instead of multiplying the examples for samples of different compositions one may deduce some useful comments on the experimental aspect from the results detailed in the above subsection. Among other effects on the emitted characteristic intensities, larger is the beam energy E° and larger are the attenuation effects at normal emergence via the increased extension into the bulk of the $\Phi(z)$ function. Conversely the decrease of E° would lead to increase the $f(\chi)$ value at normal emergence. Then for the Al K line in pure Al and in the Al-Mg alloy, Fig 4a, the $f(\chi)$ evolution would be approaching that of Fe K for a decreasing beam energy below 15 keV while their initial value, at $\theta=0^\circ$, would decrease for an increasing beam energies above 15 keV.

In fact the angular changes in intensity are a function of the exponential factor, $\exp(-(\mu z \cos \theta))$, Eq. 5, having a maximum value at normal emergence of about - (μz_X) [z_X : depth at which $\Phi(z)$ the function becomes negligible]. When (μz_X) is larger than 2-3 the absorption effects are too large for the corresponding signals to be detected even at normal emergence. Conversely when (μz_X) is less than ~ 0.1 , $f(\chi)$ is close to unity at the same normal emergence but its angular decrease is only significant near grazing θ angles. This last situation was that of the experiments of Chenai et al. for the Fe K line of pure Fe at 30 keV -Fig. 4a and [9]-. For such a multiline-element sample, one may point out that a more significant change would be obtained from a measured angular evolution of the Fe L lines at $E^\circ \sim 5$ keV: μ (Fe L in pure Fe) $\sim 1.7 \mu\text{m}^{-1}$.

Then to obtain a significant θ change and a detectable signal, the choice of E° results from a compromise and for multiline-elements this strategy may be combined to the best choice for the characteristic radiation of interest.

4° Perspectives.

This section suggests a new instrumental arrangement and the expected performance of AR-EPMA in terms of specific applications. Perspective for the developments of the technique is also given.

4°1. A suggested instrumental arrangement. The present investigation has been previously undertaken with a dedicated electron microprobe [9] as well as with a SEM that has an EDS detector [10]. As intuitively expected and also pointed out by Völkerer et al. [10], the main experimental problem is the sample positioning in the instrument. The extreme sensitivity to low take-off angles requires very exact positioning of the investigated point of the sample on a rotation axis that is aligned to the incident beam. Also the tilt angle has to be determined with high precision in order to correspond to the optimized angular conditions. Illustrated in Figure 8, a solution of this problem may be inspired from some developments in Atomic Force Microscopy (AFM) [16-18] that have been recently adapted to the corresponding marketed instruments. Like for the position of the cantilever in AFM, the position of the sample may be determined by an optical-beam-deflection system combined to a position sensitive detector and a motorized measuring sample positioning may be obtained with a positioning resolution better than 1 μ m. Acting as a closed-loop sensor the position sensitive detector permits to modify the height of two of the three pillars of a tripod on which the inclined sample is set. The change of the investigated detail of the sample may be obtained from x,y displacements driven by piezoelectric ceramics or ultrasonic transducers while same displacements permit measurements on standards set side by side to the sample. Finally the stepped motor used for the ω -rotation may be driven by a specific algorithm to explore some preselected take-off angular ranges and, overall, to increase the acquisition time when the take-off angle θ decreases, this for compensating the inherent decrease in intensity. The most important angular effects occurring when take-off angles are less than $\theta < 30^\circ$, corrections for the finite acceptance angle of the detector, $\theta \pm \Delta\theta$, must be considered for grazing emergent x-rays - practically a lower limit of 5° would be sufficient-.

Again like for many marketed AFM instruments, the whole process may be fully automatic while keeping unchanged the excitation parameters (i.e., the incident beam energy, E° , the intensity, I° , the angle of incidence, and the detector position). Obviously, flat samples are required but the close loop sensor associated to the position sensitive detector would permit slight deviations from a perfect planarity.

It may be interesting to point out that the ability to vary the take-off angle in instruments with fixed incident beams and fixed spectrometers may be transposed to many beam techniques. Then the same attachment may be implemented into Auger spectrometers for performing AR-AES, the additional requirement would be to use slits or apertures in front of the spectrometer in order to reduce its acceptance angle, $\Delta\Omega$.

4°2 Expected performance in comparison to other techniques.

The main limitations are those of conventional EPMA related to the inability to detect ultra-light elements such as Li or elements in low concentration -detection limit problem-combined to the possible overlap of neighbor x-ray lines. Then it would be easier to detect a carbon layer on a gold substrate than a carbon substrate coated by a rather thick gold layer.

As evidenced by Gennai et al.[9] with the use of a dedicated electron microprobe, the use of AR-EPMA permits to measure the absorption factor, $f(\chi)$ and the same type of experiments permits to deduce the absorption coefficients of the investigated materials instead of using tabulated values often known with a poor degree of accuracy. In addition there is the possibility to operate at a take-off angle of $\sim 90^\circ$ in order to minimize the weight of the absorption effects that have to taken into account in all the quantification procedures.

As pointed out and evidenced by Völkerer et al., [10] with the use of a SEM +EDS attachment the ratio of two measurements of the same tilted sample at different take-off angles permits to eliminate the uncertainty of some of the parameters involved in the intensity-concentration relationship, leading then to a standardless analysis by EPMA-TWIX [10]. The key argument is that in AR-EPMA are unchanged the excitation parameters (i.e., the incident beam energy, E° , the intensity, I° , the angle of incidence) and the detector position and efficiency.

Keeping unchanged the excitation parameters permits a choice of the incident beam energy, E° , only governed by the optimization of the investigated angular range (section 3°6) and it allows the large speed of acquisition of angular profiles when the above-suggested experimental arrangement is combined to a Silicon Drift Detector (SDD) as x-ray detector in a SEM. Due to the large dynamic of these modern detectors, up to 10^6 counts/sec, the automatic acquisition of an angular profile may only take a few minutes that is significantly less than the variable beam energy method.

Then the proposed approach permits a fully automatic and rapid registration of the angular profiles even for samples having depth-concentration profiles. In addition, being based on the attenuation change of a characteristic line of a given element by the presence of other

elements, it is possible to obtain some additional information on these other elements when their absorption coefficient is significantly different from that of the characteristic x-ray line of the element interest. Even when these other elements cannot be detected, the sum of the measured atomic concentrations, $\sum C_j$ ($=$ or $\neq 100\%$) would the concentration of missing (or difficult to detect) elements to be estimated: see Fig. 4b for a Al-Be alloy.

Also the speed of acquisition permits to change the investigated points along a line in order to identify differences in the corresponding z-concentration profiles. This concentration profile method may be compared to AR-XPS that is of a frequent use in surface analysis [8] [19]. The in-depth sensitivity of AR-XPS is of the order of an atomic monolayer for a maximum information depth of a few nm while, when the detected characteristic x-ray lines are of a few keV, that of AR-EPMA is of a few nm for a maximum information depth of about one micron. Nevertheless when the detected x-rays are soft x-rays, of energy below 1 keV, the in-depth resolution of AR-EPMA would be significantly improved because of their large linear absorption coefficients, μ , leading to a broadening of the useful angular range by a more significant change in the function $\mu z \csc \theta$. The parallel detection of all the collected characteristic lines would permits to simultaneously acquire different information depths of a given element when two different characteristic lines of this element are detected: e.g.: Fe K and Fe L lines where the attenuation change of the Fe L line would be more interesting than that of the Fe K line for the of the FeAl alloy investigated by Chenai et al..

The lateral resolution of EPMA is intrinsically better than that of XPS and the use of incident energies of a few keV would permit to decrease the maximum information depth of EPMA permitting then the two techniques, AR-EPMA and AR-XPS, to be complementary to each other for in-depth profiling.

To end the comparison between AR-EPMA and in-depth profiling with surface sensitive techniques such as XPS and AES one may point out the great demand of depth profiling methods that is often fulfilled by combining XPS or AES to ion milling [8]. These combined approaches lead to problems in the depth calibration and in quantification with respect to the non-destructive aspect of AR-EPMA.

4°3 Applications.

Scanning Electron Microscopy is probably the most widespread technique being used in Research & Developments laboratories and many of the corresponding instruments are equipped with an EDS attachment. Then the suggested experimental arrangement may be implemented into a large number of equipments to be applied to all fields of applications of

SEM+EDS. The potentiality of non destructive in-depth profiling of AR-EPMA opens it to many of the applications of AES depth profiling [8] [19] without the complications of ion milling. The exhaustive list of potential applications is out of the present purpose and only some selected areas are indicated here.

One obvious field of applications concerns quite all the aspects of metallurgy from the manufacturing process to the end product via failure analysis and research activity of new materials [8]. In metallurgy the starting materials are submitted to various thermal, chemical and coating treatments that modify its surface composition down the micron range or more and the interest of a rapid acquisition of z-profiles by AR-EPMA is evidence.

The glass industries are also dealing with stratified materials with, in particular, the use of optical coatings (e.g. antireflective coatings) where the thin film coating consists of multiple layers having varying thicknesses. For this type of applications involving poorly conductive materials, the advantage of EPMA over AES is the possibility to coat the sample with a thin carbon or gold layer to prevent charging effects leading to difficulties in AES analysis via the deflection of the incident beam. For such a surface film the advantage of AR-EPMA over conventional EPMA lies in the rapid control of the film thickness homogeneity.

Microelectronics is another interesting field of application of the suggested technique. The technique cannot be used to investigate multilayered devices constituting the heart of semiconducting junctions and transistors because of its too poor depth resolution but its analytical properties may be used for quite all the other steps of the manufacturing process: inspection, packaging and failure analysis. An extensive list of problems being solved from the use of SEM+EDS and of AES may be founded in ref. [20] and most of them may also be solved more rapidly with AR-EPMA. .

4°4 Further developments.

In fact the main goal of the present contribution is to attract the attention of the microbeam analysis community on the new potentialities of AR-EPMA in order to incite it in the building of the suggested attachment for fast routine analysis, first.

In parallel or in continuity to this experimental step, more sophisticated quantification procedure would be established by experts in this field. The theoretical developments of Section 3 are given only as an outline of the expected performance of the suggested approach. For this restricted goal, the characteristic photon energies of interest have been limited to the 1-2 keV range for materials of rather low absorption coefficients. Such a choice limits the useful angular range of the take-off angles. It is clear that the collection of softer x-rays,

below 1 keV, having larger linear absorption coefficients, μ , would broaden the useful angular range by a more significant change in the function $\mu z \csc \theta$. This energy range is not investigated here and the readers are referred to the review paper of Love & Scott for the specificities of this photon energy range in conventional EPMA [21]. The field of theoretical investigation of the expected performance is widely open for a large variety of compounds of different x-ray characteristic energies. Also for the sake of simplicity, the present evaluation is based on the use of a $\Phi(z)$ function that holds for a normal incidence. For the future for quantitative analysis at a non-normal incidence, the best choice of this function would be inspired by the extensive works of Bastin et al. [22] among others.

In EPMA, the precision of the quantification procedure depends greatly on the precision of the values of the absorption coefficients, μ . Unfortunately, the tabulated values [11][12] present a rather large dispersion. The best approach seems to be an experimental determination with the suggested equipment. From the measured angular profiles, the best fit for μ would be deduced from the insertion of the best $\Phi(z)$ function into Eq. 3. Nevertheless, by choosing $\theta = 90^\circ$, the suggested equipment permits one to minimize the absorption effects in the investigation of homogeneous samples.

As for more conventional approaches, the present approach needs to take into account the fluorescence effects by classical fluorescence corrections. At grazing emergences of $\theta < 10^\circ$, a correction of the refraction effects may also be considered the present method offers the advantage of keeping the excitation parameters constant (i.e., beam energy and intensity, angle of incidence). In the end, the reconstruction of in-depth profiles from the experimental angular profiles may benefit from the results of Laplace transform inversion, such as those obtained in angle-resolved XPS [19].

5° Conclusion.

In continuity to the pioneering works of Chenai et al. [9] and of Völkerer et al. [10], the present contribution proposes the implementation of a new sample attachment in dedicated electron microprobes and in SEM equipped with an EDS detector. The goal of this arrangement is to change the take-off angle in order to change the attenuation of characteristic x-rays and, then, their information depth in a way similar to that in AR-XPS. This will be based on the change in the attenuation of characteristic x-rays (Section 2), while keeping the excitation conditions unchanged. This attachment may also be implemented in any kind of instrument that has fixed incident beams and fixed spectrometers, such as Auger instruments. This attachment permits the automatic acquisition of angle-resolved intensity profiles, which

may be converted to in-depth concentration profiles. The expected performance of such an attachment has been evaluated for three neighboring elements, Mg, Al and Si, that are involved in various samples - homogeneous alloys and stratified samples- (Section3). One of the main advantages of the suggested arrangement is the rapid acquisition of the intensity profiles (Section 4).

Final remarks. This article has been written in memory of Professor R. Castaing at the occasion of the 90th anniversary of his birth.

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Figures

Figure 1 a. Schematic diagram of the sample set up. Central part: ON: normal to the sample surface, OD: direction of the collected signals, *i*: incident angle, *d*: detection angle.

For the inclination of the sample, the simplest solutions are: $i=d$ (where $\theta=90^\circ$ when ON is confused with OD) and $i=90^\circ-d$ (where $\theta\sim 0^\circ$ when a direction O(T) in the sample plane is confused with OD). ω : rotation angle eventually driven by a stepped motor, S.M.. *x*, *y*, *P*: *x*,*y* positioning stage. Left and right parts: Extreme situations: $\theta\sim 0^\circ$; $\theta=90^\circ$. **b.** Correlation between ω and θ when $i=d$ and –between parentheses- when $i=90^\circ-d$. Simplified geometry and –between parentheses- when $i=90^\circ-d$. **c:** Numerical applications of Eq. 1 or Eq; 1' for the correlation of the rotation angle, ω , and the take off angle, θ .

Figure 2. Inspired from [10][11], evolution as a function of the photon energy, $h\nu$, of the photo-absorption cross sections of Mg, Al and Si: Q_{Mg}^x , Q_{Al}^x , Q_{Si}^x , - unit 10^{-20} cm^2 -. $Q_{Be}^x(h\nu)$ is also shown for a comparison.

Figure 3. Calculated influence of the take-off angle θ on the function $\Phi(z) \exp(-\mu z \csc \theta)$ for Al K_α photons generated into pure Al, **a**, and into a 50% atomic Al/Mg alloy, **b**.

In **a**, the full line corresponds to only $\Phi(z)$ of a Gaussian form simulated with a fit of the ‘experimental’ $\Phi(z)$ function, symbols, of Castaing and Descamps [15], the Gaussian curve being: $2.3 \exp[-(z-0.6)^2/0.85]$. In **b**, the curves are derived from Eq. 5 with $C_{Al}=50\%$ and $\mu=0.5(\mu_{Al}+\mu_{Mg}) \sim 0.576 \mu\text{m}^{-1}$. z_x is the depth at which the function $\Phi(z)$ becomes negligible. Note the decrease of the maximum x-ray escape depth, R_x , from $\sim 2 \mu\text{m}$ for $\theta \sim 90^\circ$ down to $\sim 1 \mu\text{m}$ for $\theta \sim 15^\circ$ –dashed straight lines- .

Figure 4. a: Evolution of the absorption factor, $f(\chi)$ as a function of θ for Al K_α issued from a pure Al sample and from a 50% atomic Al/Mg alloy compared to the experimental results obtained by Gennai et al. [9] for Fe K_α radiation propagating into pure Fe and into a Fe-Al_{24%wt} alloy. **b:** Evolution of the K ratio as a function of θ for Al K_α and Mg K_α issued from a 50% atomic Al/Mg alloy. In addition, the upper curve shows the evolution of the K ratio as a function of θ for Al K_α issued from a Al_{90% at.} Be_{10% at.} alloy.

Figure 5. Evolution of the K ratios for a stratified sample, Al/Mg/Si, composed of two layers, 0.5 μm each, on a substrate. The composition of the two layers and the substrate are all different- see top insert-. **a:** the radiations of interest, respect AlK_α ; MgK_α ; SiK_α ; are issued from the top overlayer. **b:** the same radiations of interest are issued from the substrate.

Figure 6. Similarly to Fig. 5, evolution of the K ratios for a stratified sample, Al/Mg/Si, for a 0.5 μm layer sandwiched between a top layer and a substrate, each having a different composition.

Figure 7. Gaussian concentration profile: Mg/Al alloy. **a:** postulated concentration profile of Mg in aluminum. **b:** angular evolution of the K ratios for AlK_α and MgK_α . The case of a $\text{Al}_{72\%}$ at $\text{Mg}_{28\%}$ at homogeneous alloy is given as a comparison.

Figure 8. Suggested experimental arrangement.

Table I . K and K_{twix} for some overlayers on Si substrates; Si K_{α} line; $E^{\circ}=20$ keV; $15^{\circ}\leq\theta\leq55^{\circ}$.

K_{twix} (Exper.): experimental values given in [10]. K_{twix} (Calc.); K (55°) and K (15°): results of present calculations.

overlayer	Al	Au	Cu	Al	Al	Cu	Cu	Pd	Co	Cu
t (nm)	8.5	3.	10.	42.	67.	26.	50.	90.	100.	120.
μt	0.0075	0.00909	0.029	0.037	0.058	0.0754	0.145	0.204	0.234	0.348
K_{twix} (Calc.)	1.38	1.39	1.458	1.49	1.574	1.648	1.98	2.32	2.506	3.388
K_{twix} (Exper.)	1.34	1.336	1.419	1.455	1.56	1.618	1.978	2.241	2.553	3.588
K (55°)	0.990	0.988	0.965	0.956	0.932	0.912	0.838	0.78	0.752	0.654
K (15°)	0.971	0.965	0.894	0.867	0.799	0.747	0.571	0.455	0.405	0.260

a

b

c

Figure 1

Figure 2

a

b

Figure 3

a **b** **Figure 4**

a **b** **Figure 5**

a **b** **c** **Figure 6**

a

b

Figure 7

Figure 8