# Technical Note #4

## X-Ray Induced Auger Peaks and Their Usefulness

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### Theory

Following the formation of a core hole through photoelectron emission, the now excited system will act to return to a more neutral state by an outer shell electron filling the vacancy. This releases a discrete amount of energy which may be passed to another electron causing its emission – the Auger electron.

The core hole produced during photoemission can be rapidly neutralized by an outer shell electron from a higher level. This transition leads to a release of energy which may be removed from the system as a photon (fluorescence) or through the emission of a secondary electron in a radiationless transition known as the Auger process; the probability of which dominates can be related to the atomic number (*Z*) of the emitting atom.

Figure 1 shows an example of the Auger emission for metallic nickel. Photoionization leads to a hole in the $2p_{3/2}$ level which is filled by an electron from the 3*d* shell, which is accompanied by the emission of an electron from the 3*d* shell. For historical reasons, Auger transitions are described using x-ray rather than spectroscopic notation and the process shown in figure 1 is termed a $L_3M_{45}M_{45}$ transition. The energy of the Auger electron $E_{LMM}$ depends only on the energies of the orbitals involved and is given by equation (1), where * represents the presence of a hole in $M_{45}$

$$E_{LMM} = E_{L3} - E_{M45} - E_{M45*} \quad \text{..... (1)}$$

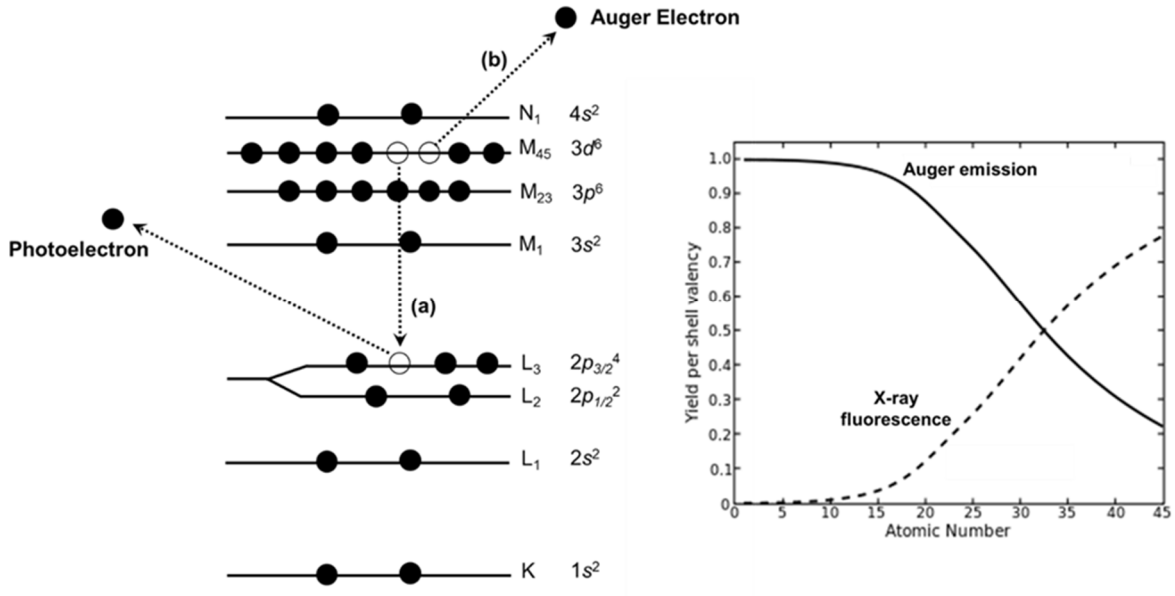


**Figure 1.** Energy level diagram for the neutralization of a core hole (step (a)) accompanied by the emission of an Auger electron (step (b)) for nickel metal. A plot illustrating the variation of Auger electron and fluorescence yields with atomic number Z is also shown (Reproduced with permission from [1])

## The Usefulness of Auger Peaks and the Auger Parameter

X-ray induced Auger spectra have quite unique (and sometime complex) peak shapes and positions but are very useful in the determination of chemical state analysis, and confirming elemental identification.

Wagner derived the so-called Auger parameter ($\alpha$), which is useful for chemical state analysis and is independent of surface charging [2, 3]. Calculation of the Auger parameter as originally defined by Wagner is giving in equation (2).

A calculated value from both photoelectron and Auger peak positions is the Auger parameter ($\alpha$). This parameter is particularly useful for chemical state analysis and can be used without interference of surface charging. Originally defined by Wagner [1,2], the Auger parameter is calculated as follows:

$$\alpha = E_k(C_1C_2C_3) - E_k(C) \quad \text{..... (2)}$$

where $E_k(C_1C_2C_3)$ is the kinetic energy of the Auger transition involving electrons from $C_1$, $C_2$ and $C_3$ core levels and $E_k(C)$ is the kinetic energy of the photoelectron from core level C, the drawback of the equation in this form is that it allowed for negative values of $\alpha$. In light of this, the modified Auger parameter ($\alpha'$) was introduced by Gaarenstroom and Winograd [4] by addition of the photon energy to $\alpha$. Independent of the incident X-ray energy used the modified Auger parameter is calculated as follows:

$$\alpha' = E_k(C_1C_2C_3) + E_b(C) \quad \text{..... (3)}$$

where $E_b(C)$ is the binding energy of the core level C. Since any surface charging shifts will be of the same magnitude, but of opposite direction in each of these two components, they will be automatically cancelled out in $\alpha'$. This modified Auger parameter is that which is commonly used.

## Chemical State Plots (Wagner Plots)

A scatter plot of the most intense photoelectron line binding energies (abscissa, oriented in the negative direction) *vs*. the kinetic energy ($E_k$) position of the sharpest $C_1C_2C_3$ Auger line (ordinate) is typically known as a chemical state plot or a Wagner plot. Positions of compounds on these plots indicate both relaxation energy and initial state effects [5, 6]. Hence, the modified Auger parameter can be used in addition to the binding energy envelope to give additional insight into the shift in electronic state between transition metal compounds.

The use of such Wagner plots and Auger parameters are plentiful in the literature, with examples including nickel [7], copper and zinc [5]. The online NIST database [8] contains a large collection of Auger parameter values as does the Handbook of X-ray Photoelectron Spectroscopy [9].

An example of such a plot is given in Figure 2 for arsenic species.

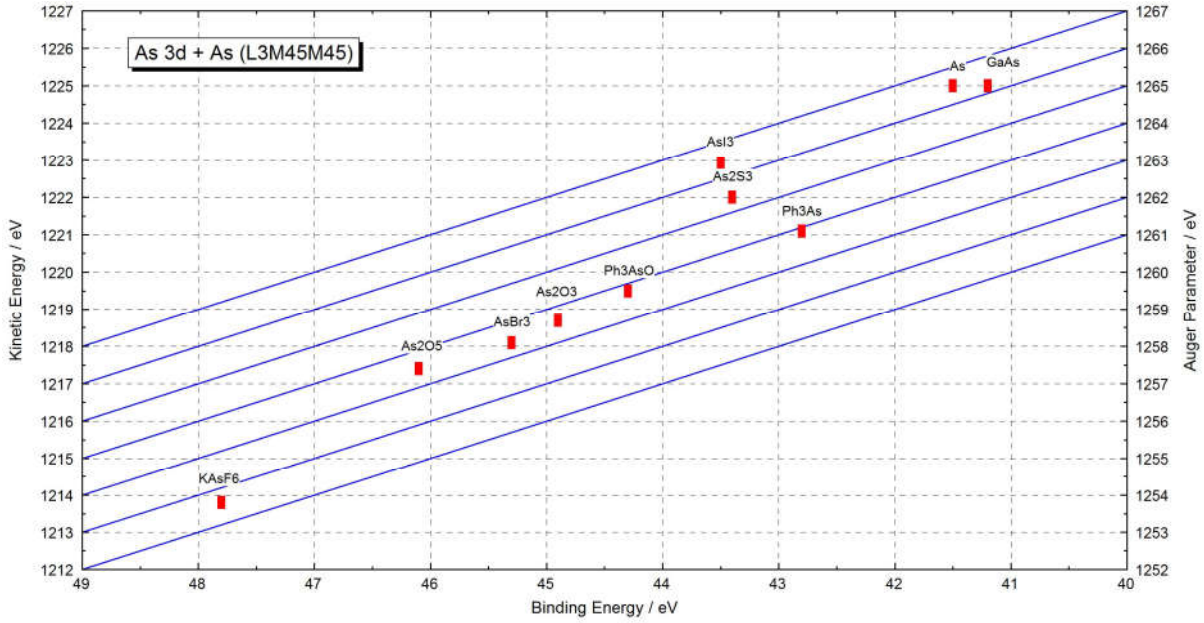


**Figure 2.** Wager plot for a series of arsenic (As) compounds

**References**

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