Zinc and Cadmium:
XPS Chemical State Determination Using Auger Parameters and Auger Peak Curve-Fitting Procedures

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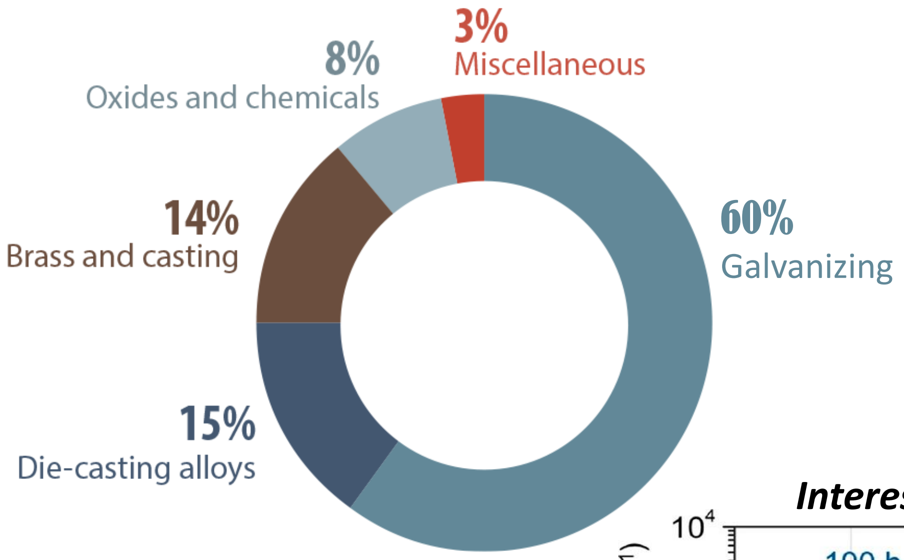
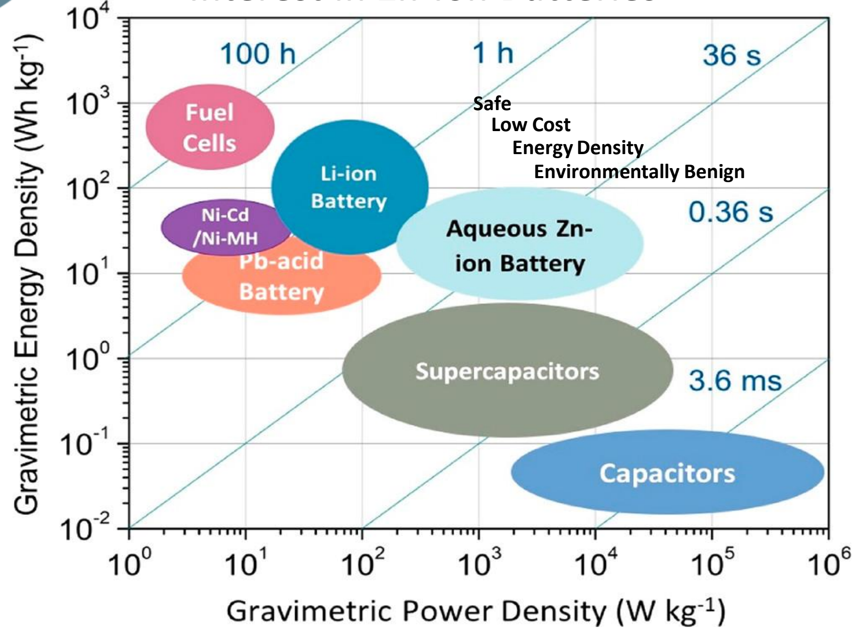
Why Zinc and Cadmium?



Global Uses of Zinc[1]

Interest in Zn-Ion Batteries[3]



Zinc

- **~ 13 million metric tons** produced globally in 2022[1]
- **4th most produced metal** in the world[2]
- Market **demand expected to exceed production** capabilities in the coming years!

Cadmium

- **~ 24 000 metric tons** produced globally in 2022[1]
- **>5%** of the global **solar cell market**[4]

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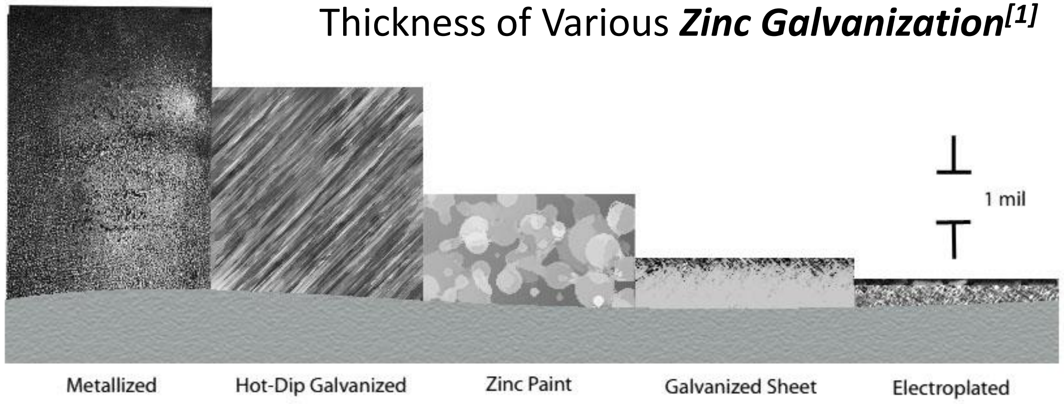
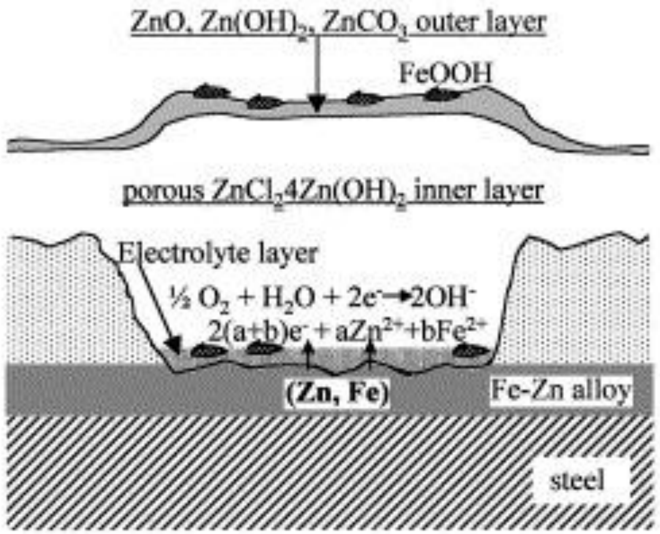
[1] Mineral Commodities Summaries 2023. United States Geological Survey https://pubs.usgs.gov/periodicals/mcs2023/mcs2023.pdf
[2] Zinc Statistics and Information | U.S. Geological Survey (2021). https://www.usgs.gov/centers/national-minerals-information-center/zinc-statistics-and-information.
[3] Jia, X. et al. Chem. Rev. 120 (15) 2020, 7795-7866.
[4] Solar Technologies Office – Cadmium Telluride. Office of Energy Efficiency and Renewable Energy. (2023) https://www.energy.gov/eere/solar/cadmium-telluride

Zinc on Surfaces

Thickness of Various ***Zinc Galvanization***[1]



Various Corrosion Processes[2]



Forms of Zinc on Surfaces

- Different forms of **zinc coatings**
- **Corrosion** by-products
- **Contaminants**
- Zinc **alloys**

A similar story is true for Cadmium

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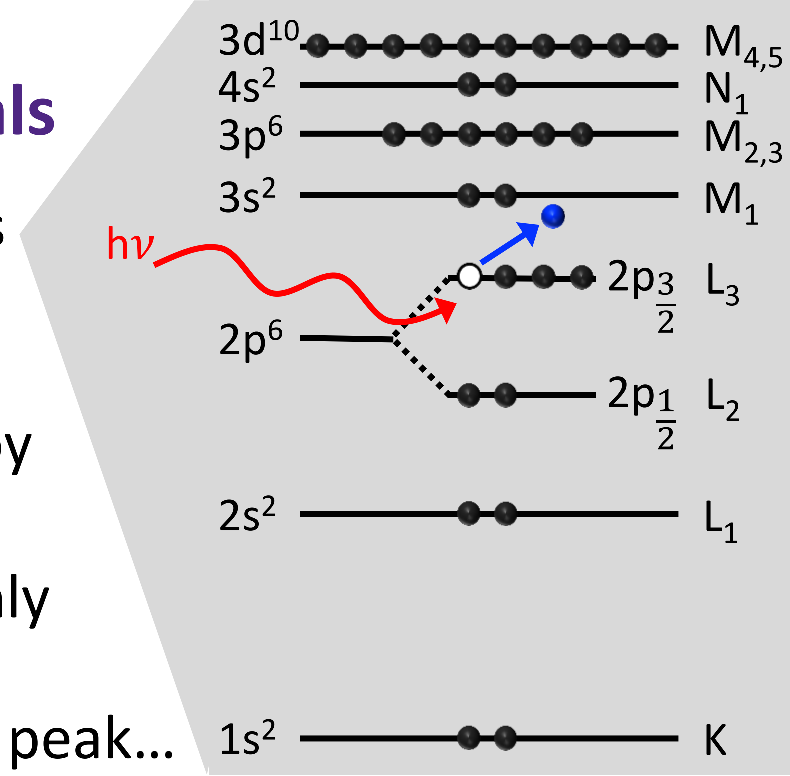
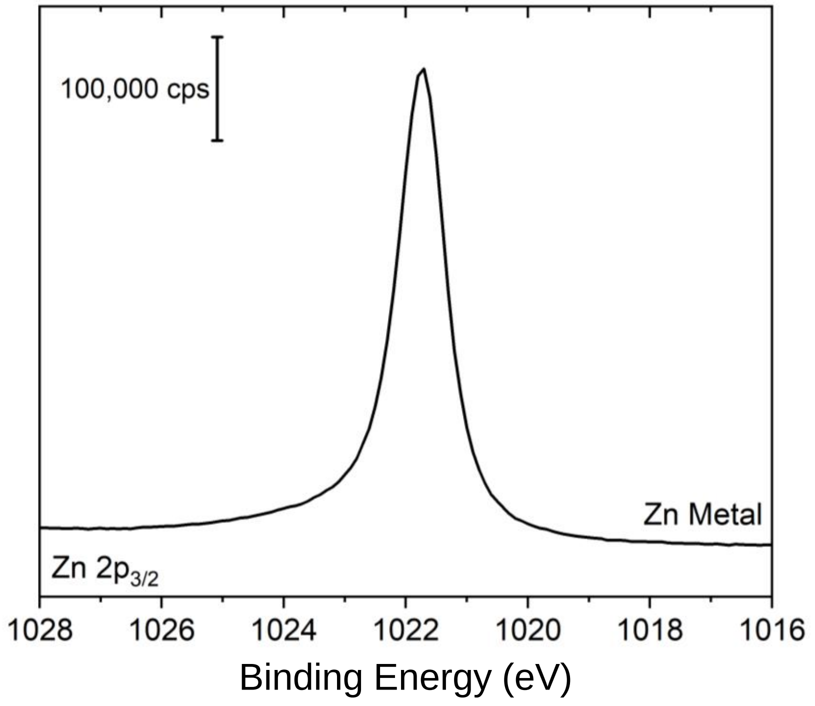
[1] Zinc Coatings (Online Publication) American Galvanizers Association (2011). https://www.galvanizeit.org/uploads/publications/Zinc_Coatings.pdf
[2] Yadav, A.P. et al. Corr. Sci. 46 (2) 2004, 361-376.

Speciation by XPS

Photoelectron Signals

- **One-electron** process
- **For many elements…** speciation achieved by consideration of the photoelectron line only
- Consider the Zn $2p_{3/2}$ peak…





Speciation made difficult due to overlap.
Cannot use this peak alone to differentiate.

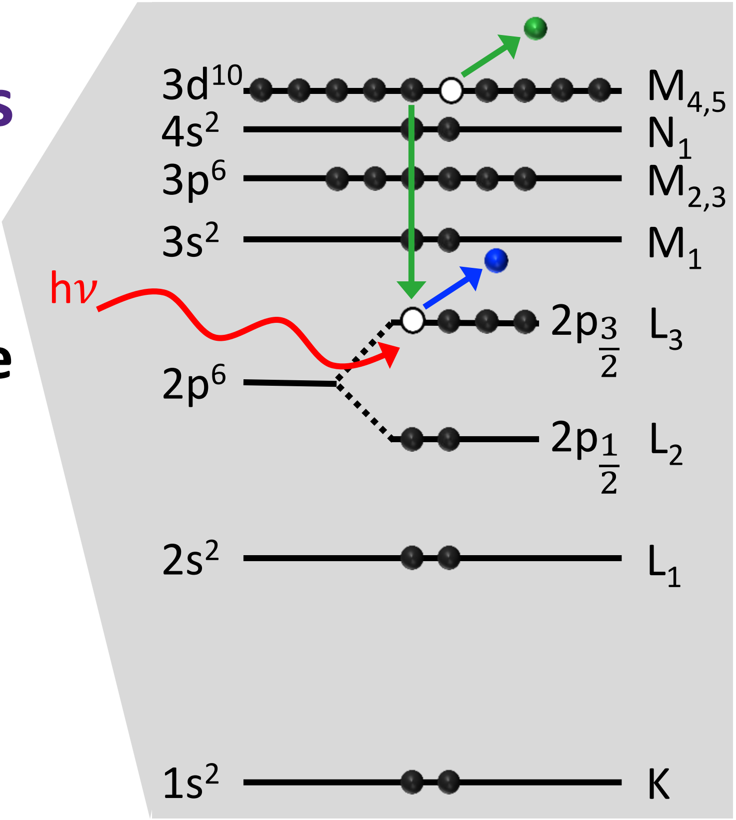
Sample	Zinc $2p_{3/2}$ Binding Energy / eV			#
Zn Metal	1021.7	±	0.3	15
ZnO	1021.8	±	0.5	13
$Zn(OH)_2$	1022.4	±	0.5	4
ZnF_2	1022.2	±	0.7	3
ZnS	1021.9	±	0.2	4
$Zn_5(CO_3)_2(OH)_6$	1022.2	±	0.4	2

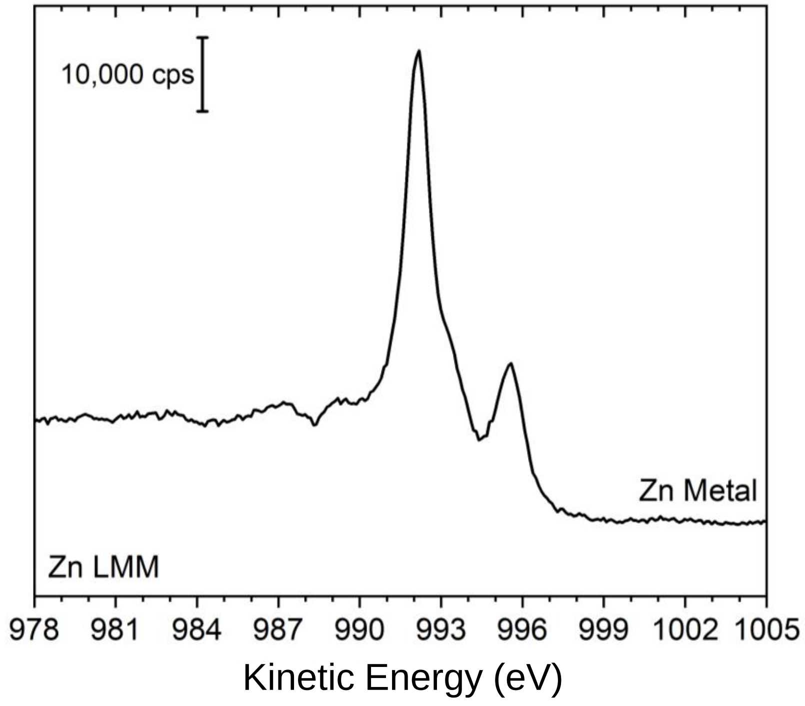
Spread of only 0.7 eV (1021.7 –1022.4 eV)

Speciation by XPS

Auger Electron Signals

- **Three-electron process**
- Auger lines have **unique shapes** and **positions**
- Consider the Zn LMM signal…





More information available when considering Auger signals!

Sample	Zinc $L_3M_{4,5}M_{4,5}$ Kinetic Energy / eV			#
Zn Metal	992.2	±	0.2	15
ZnO	988.4	±	0.6	13
$Zn(OH)_2$	987.2	±	0.5	4
ZnF_2	986.3	±	0.4	3
ZnS	989.7	±	0.4	4
$Zn_5(CO_3)_2(OH)_6$	987.5	±	0.6	2

Spread of 5.9 eV (986.3 – 992.2 eV)

Speciation by XPS

Auger Parameter, α'

- Originally proposed by Dr. Charles Wagner[1] and later modified

$$\alpha' = E_K(Auger) + E_B(Photoelectron)$$

- Useful for chemical state analyses
- Avoids interference of surface charging (*i.e.*, same magnitude / opposite in direction)

Sample	Auger Parameter Kinetic Energy / eV			#
Zn Metal	2013.9	±	0.2	15
ZnO	2010.2	±	0.2	13
$Zn(OH)_2$	2009.5	±	0.3	4
ZnF_2	2008.4	±	1.1	3
ZnS	2011.6	±	0.3	4
$Zn_5(CO_3)_2(OH)_6$	2009.7	±	0.1	2

Wagner (Chemical State) Plots

- Highlights the E_K of Auger peak, E_B of photoelectron peak, and the Auger parameter in a compact format.
- Useful tool to understand trends for a series of related compounds

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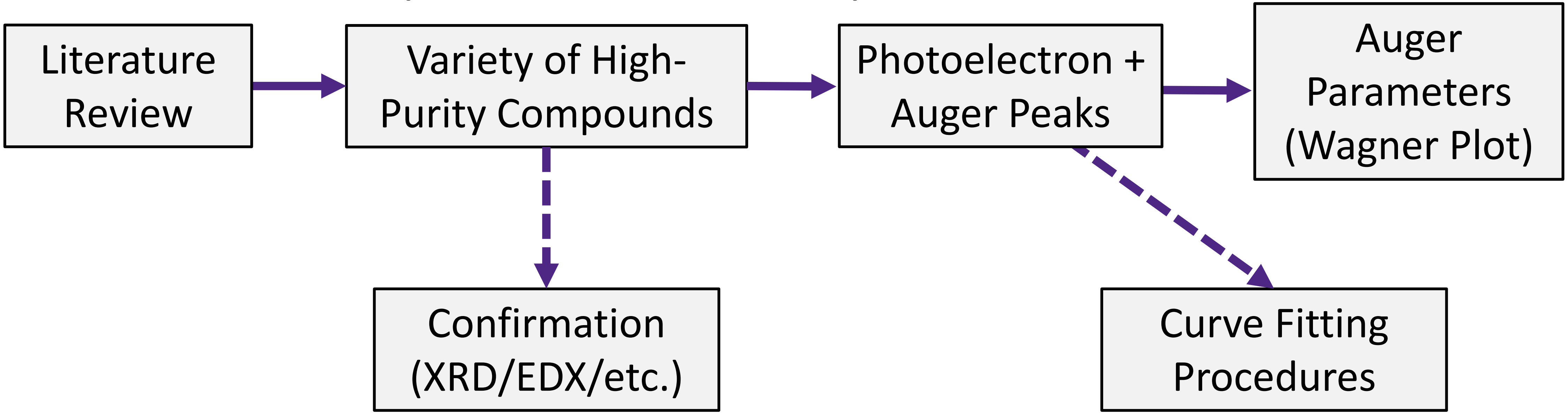
[1] Wagner, C.D., *Anal. Chem.* 44 (6) 1972, 967.

Project Motivation

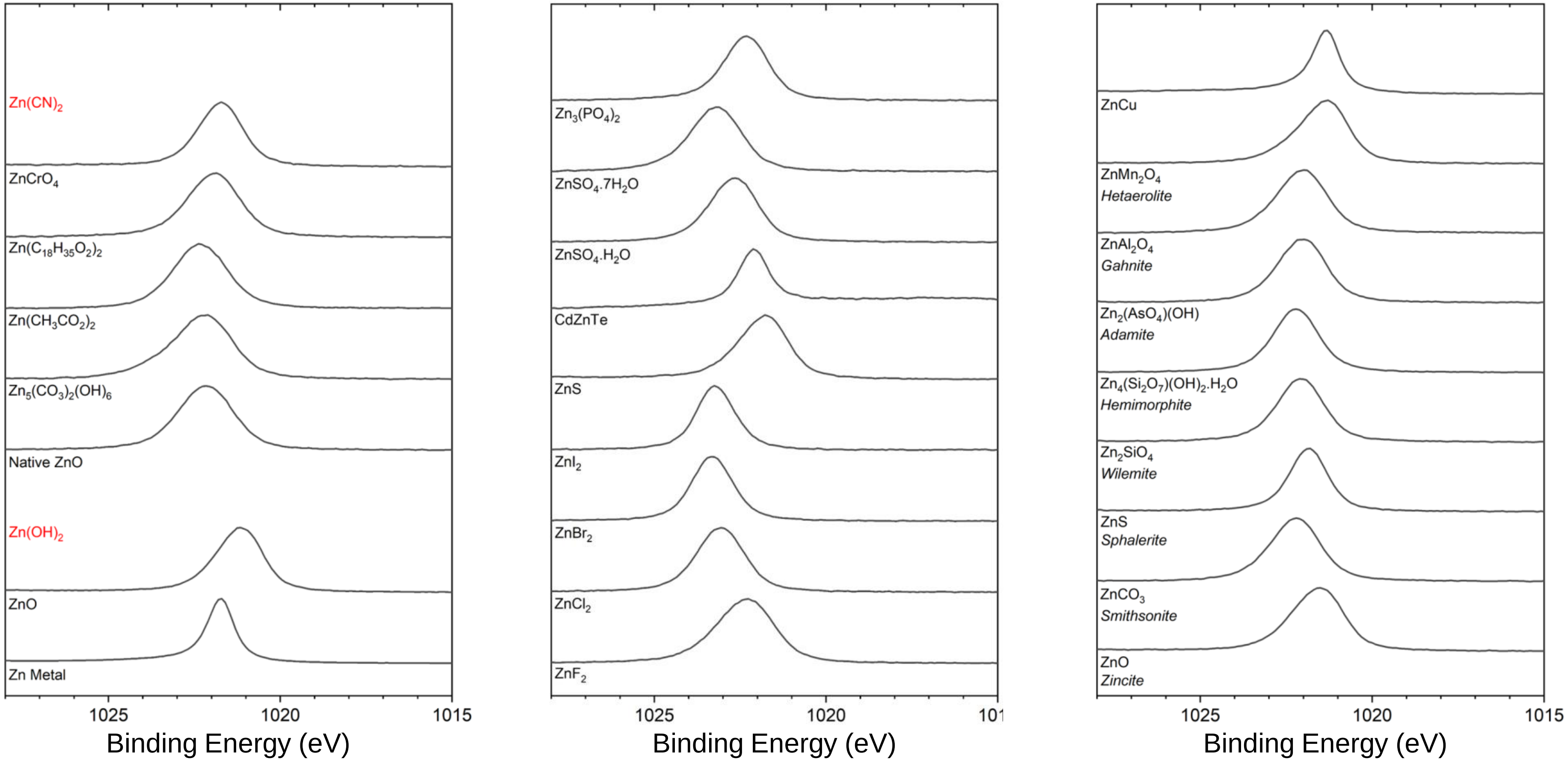
- Issues of reproducibility, consistency, and completeness in the literature
  - ➢ Only good data for **Zn metal** and **Zn oxide**

Goal: To provide **accurate**, **reproducible**, and **comprehensive** reference data to aid in the speciation of zinc compounds and minerals.



Standard Samples – Zn $2p_{3/2}$

- 27 zinc compounds and 13 cadmium compounds considered
- Limited Information available from this signal alone



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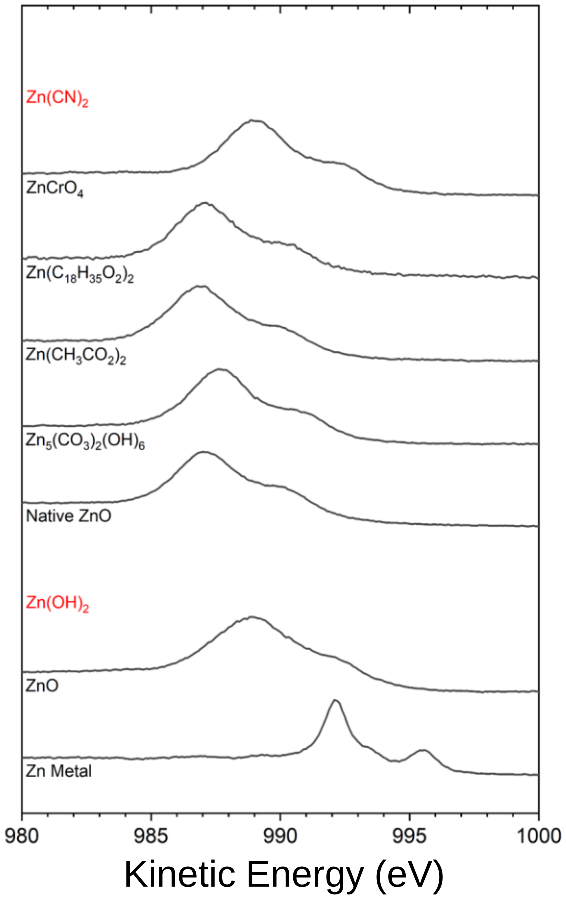
* To be completed

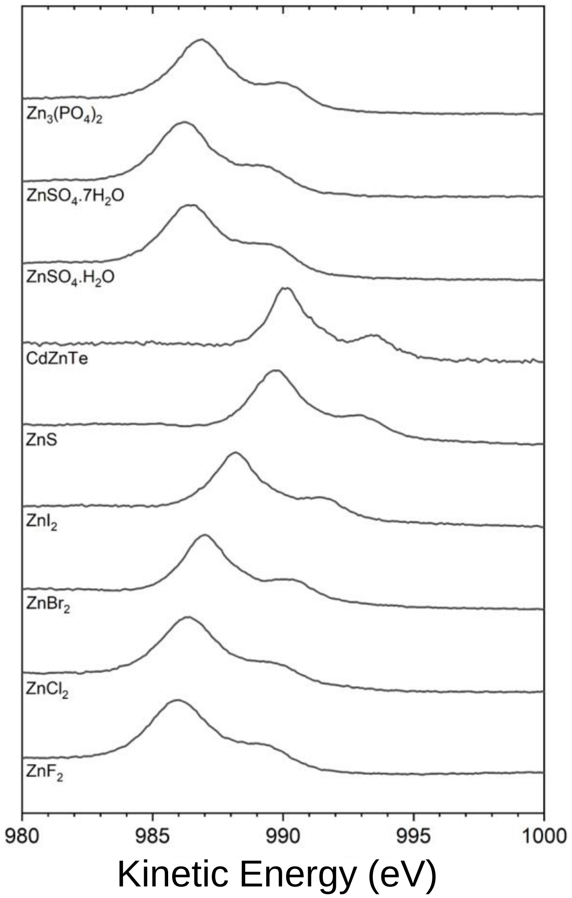
Standard Samples – Zn LMM

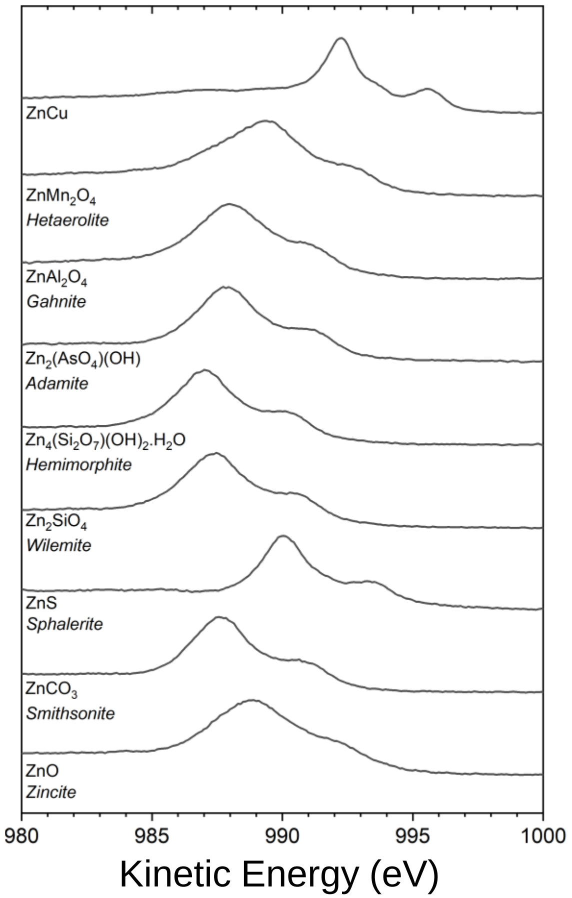
- Larger amount of information available from this signal!

Wider energy range than $2p_{3/2}$

Characteristic shape → Deconvolution







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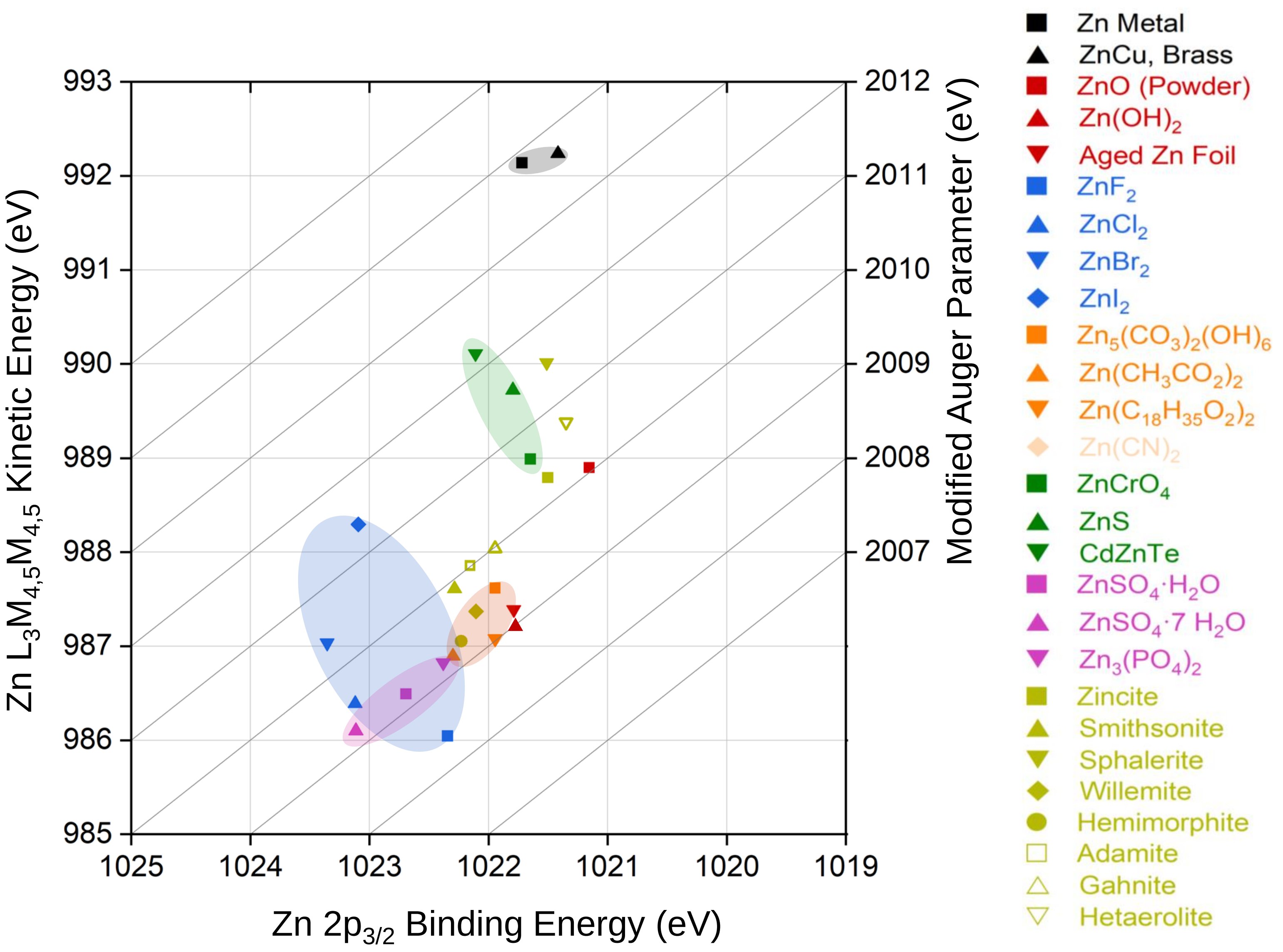
* To be completed

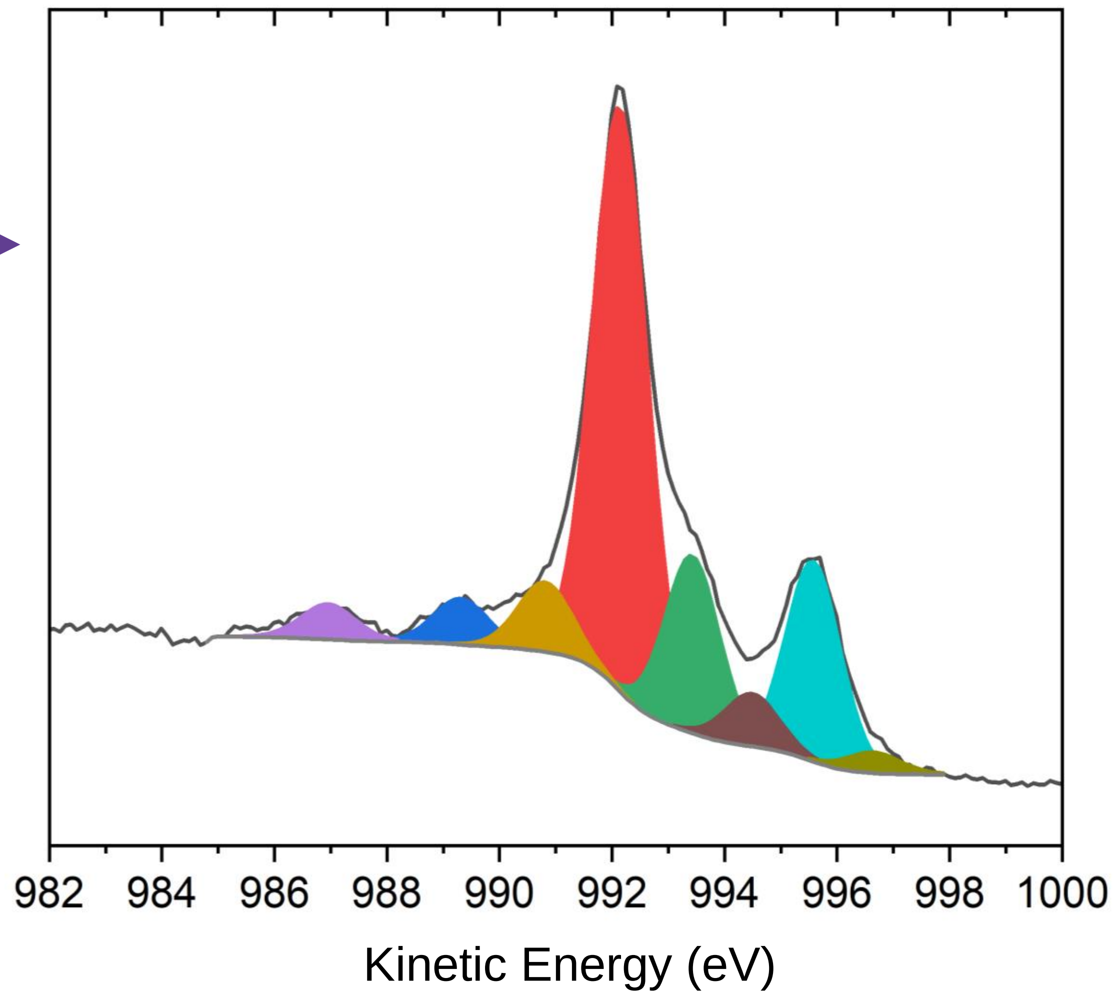
Wagner Plot

- Consider the zinc Wagner plot
- Each data point represents average over three **triplicate measurements**.
- Trends become easily observed



Mixed Species Systems

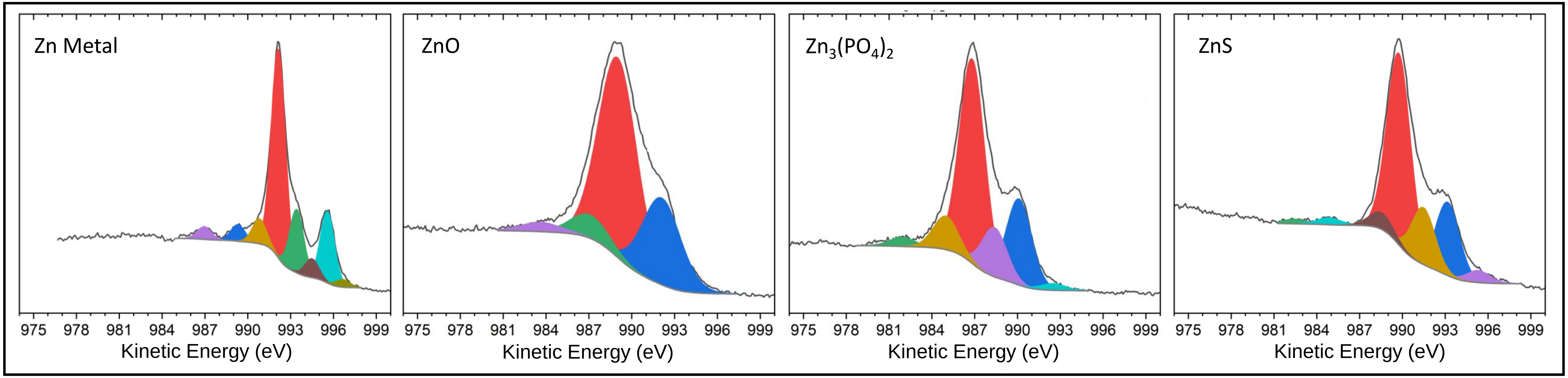
- Establishing method of curve fitting
- Consider the Zn $L_3M_{45}M_{45}$ signal for **Metallic Zinc**
- Series of individual peaks used to reproduce the $L_3M_{4,5}M_{4,5}$ envelope
- Proper peak **constraints** must be defined in order to maintain the integrity of this characteristic shape.



Constraints are key!

Curve Fitting Procedures

- Consider the $L_3M_{4,5}M_{4,5}$ signal for a series of Zn species

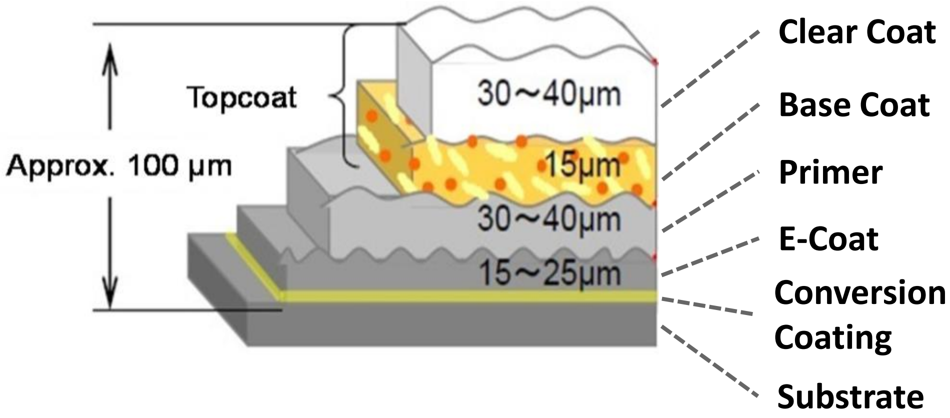


- Development of the necessary information to replicate LMM peak shapes
- Information from counter ions and stoichiometry **must** also be considered to increase confidence!

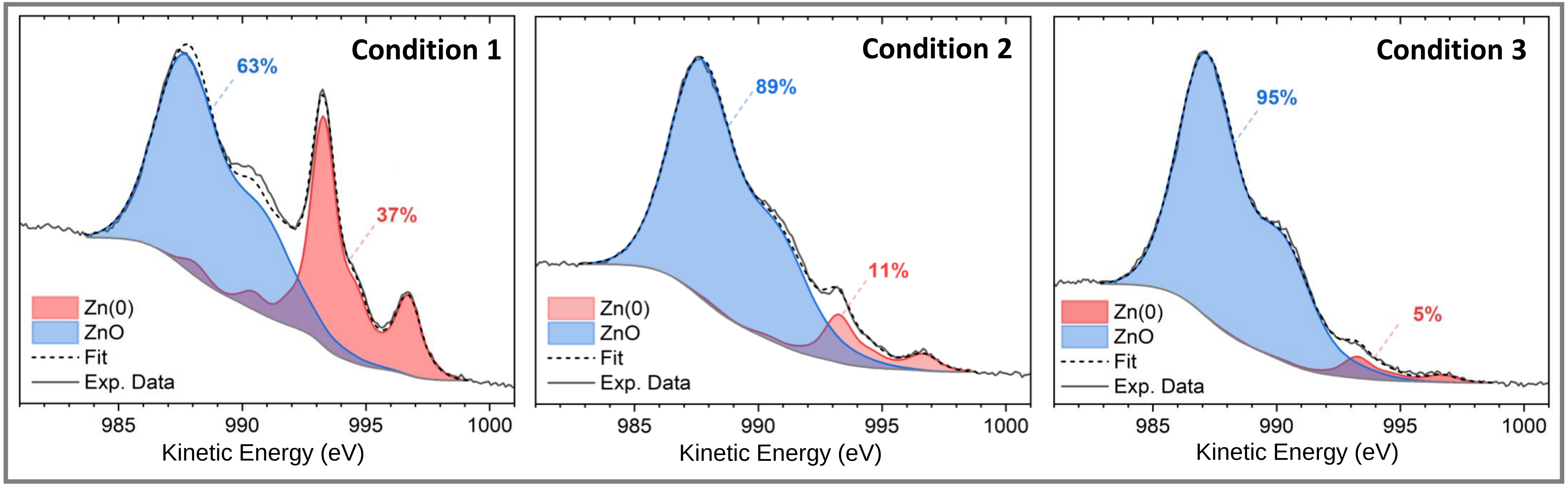
Quantifying Changes in Surface Chemistry

- Company experiencing **cohesive failure** between coating layers due to excess oxide growth

Goal: *Modify conditioning stages to minimize oxide growth before paint and coating stages.*



- Consider the surface of **hot dipped galvanized steel:**



Summary & Acknowledgments

- Accurate speciation of Zn and Cd with XPS should consider:
  - ➜ Binding Energy of **Zn $2p_{3/2}$ / Cd $3d_{5/2}$**
  - ➜ Kinetic Energy of **Zn LMM / Cd MNN**
  - ➜ **Modified Auger Parameters**
  - ➜ Information from **Counter Ions**
  - ➜ Survey quantification and **stoichiometry**
- Mixed species systems can be quantified using careful **peak fitting procedures**

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