

# Deleterious Metals & Their Impact on Splitting Limits & Assay Exchanges for Gold Dore

By: Dave Murray



# Today's Presentation

- Review of Splitting Limit Principals.
- A quick review of 2 previous papers presented at prior LBMA Assaying and Refining Conferences.
- A comparison analysis of two similar mine feeds.
- How does the presence of arsenic and or lead effect the use of the Significant Difference technique to determine the splitting limit?

# Today's Presentation

- Application of the Significant Difference technique to these two materials based on real data experience.
- What are some of the issues observed.
- The need to focus on sampling.
- Benefits of using the Significant Difference technique.
- Conclusion

# Splitting Limit Review

- The splitting limit is the percentage band in which when comparing a Client's assay to the Refiner's the average of the two assays will be used as the basis of settlement.
- When outside this percentage band, a third analysis is performed by an independent umpire laboratory.

# Splitting Limit Review

- Most often the splitting limit is contractually “negotiated”.
- Almost becoming a commercial term.
- Maybe just based on historical contracts or perceptions of risk with higher metal prices.
- Quite often very little consideration of “process capability”.

# “Statistics and Splitting Limits: Review of Au Fire Assay”

- Paper by J. Forrest, M. Hinds, and M. Theron – 2015
- To calculate the splitting limit, they used a re-arrangement of the Student’s t-test:

$$t_{calc} = \frac{(\bar{x}_1 - \bar{x}_2)}{S \sqrt{(\frac{1}{n_1} + \frac{1}{n_2})}}$$

$$\bar{x}_1 - \bar{x}_2 = t_{tab} S \sqrt{(\frac{1}{n_1} + \frac{1}{n_2})}$$

Where:

$\bar{x}_1 - \bar{x}_2$  shows a significant difference between two averages or “splitting limit”

$n_1$  and  $n_2$  are the number of replicates for the averages.

S = standard deviation; assume same for both averages

$t_{calc} = t_{tab}$  at point of significant difference – see the Student’s t-table for values based on the number of degrees of freedom.

## “Statistics and Splitting Limits: Review of Au Fire Assay”

- The paper was spurred by requests by customers and others to see splitting limits tightened.
- Not always a lot of consideration given to the nature of the material being sampled and assayed.
- To produce a statistical guideline to do a sanity check on a proposed splitting limit.

## “Sampling, and the Determination of Au and Ag by Fire Assay in the Presence of Fe and Ni”

- Presented at the 2019 LBMA Refining & Assaying Conference.
- Spoke to the issue of various impurities in material sent for refining and their impact on the ability to both obtain representative and homogenous samples.
- The paper particularly focused on the difficulties of producing good assays from materials rich in iron and nickel in the presence of silver.



## “Sampling, and the Determination of Au and Ag by Fire Assay in the Presence of Fe and Ni”

The main issue with these impurities is that:

Large enough percentages, create significant segregation in the melt and samples.

Their presence increases the uncertainty of the measurement.

This can lead to a significantly **low** or **high** credit for the precious metals present.

## “Sampling, and the Determination of Au and Ag by Fire Assay in the Presence of Fe and Ni”

Iron and nickel do not effectively alloy with silver.

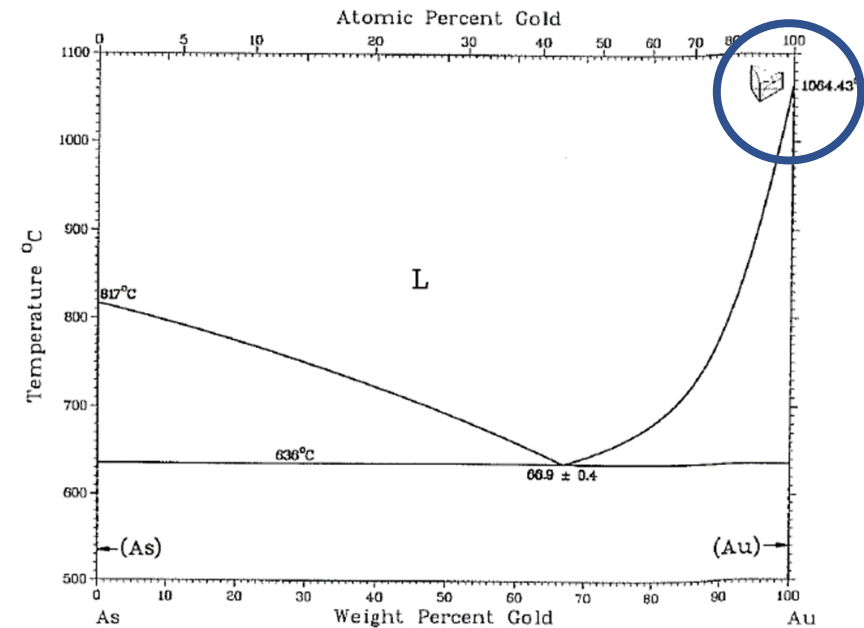
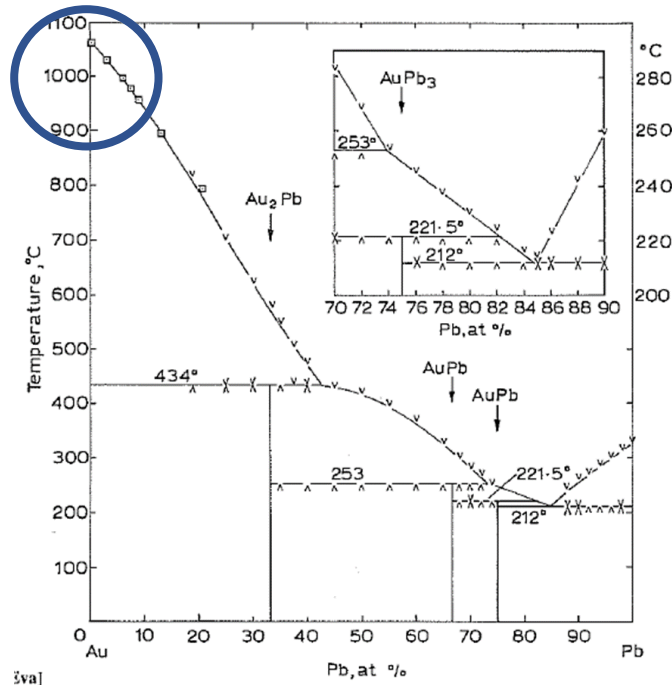
In the case of iron this is “not at all”.

In the case of nickel and silver they only alloy when they are present as small %'s of the mix with the other.

When present in a gold and silver lot they present challenges for both sampling and assaying.

# Other Metals Creating Issues

- Two other common problematic metals present in many materials coming from mines are arsenic and lead.



H. Okamoto and T.B. Massalski, 1984.

Figures from Okamoto & Massalski

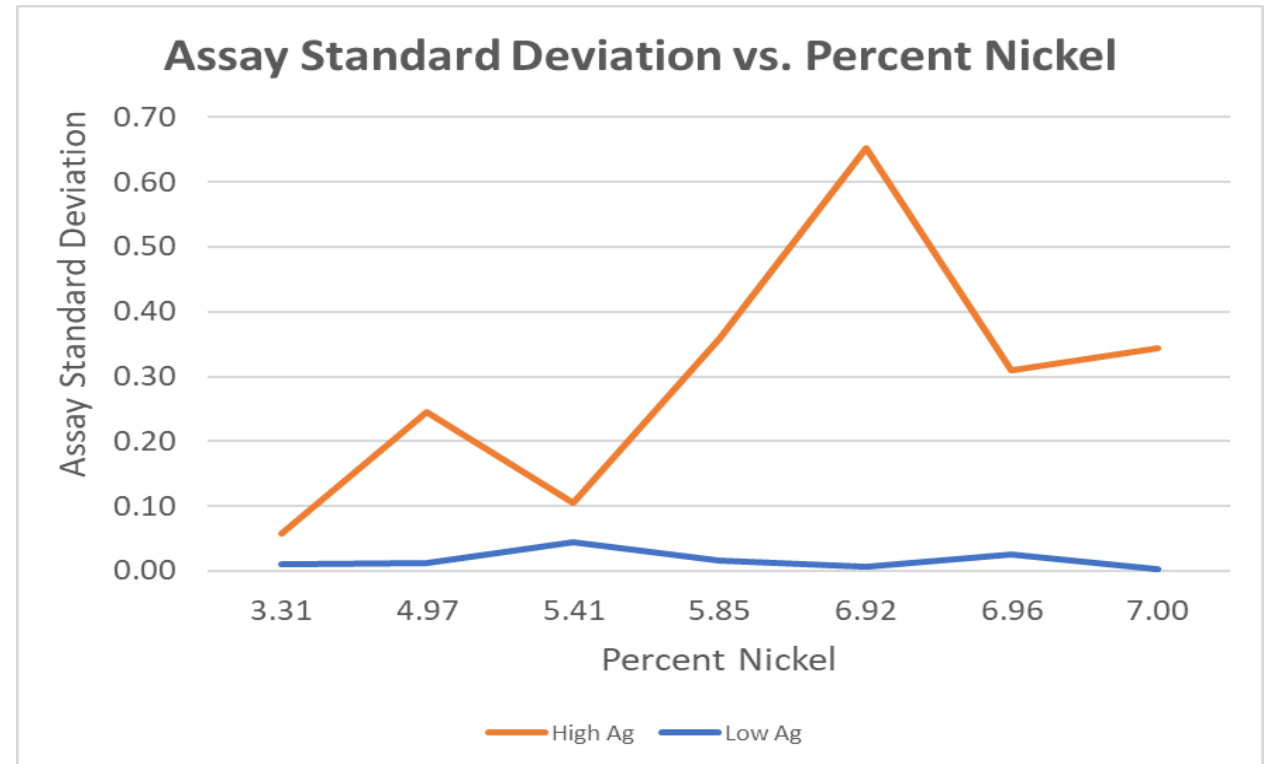
# Comparison of Two Mine Feeds

- Both mines owned and operated by the same company.
- Similar grade of gold and silver content (~80% Au).
- However, one mine 3% arsenic and 0.65% lead.
- Second mine trace arsenic, and 0.08% lead.



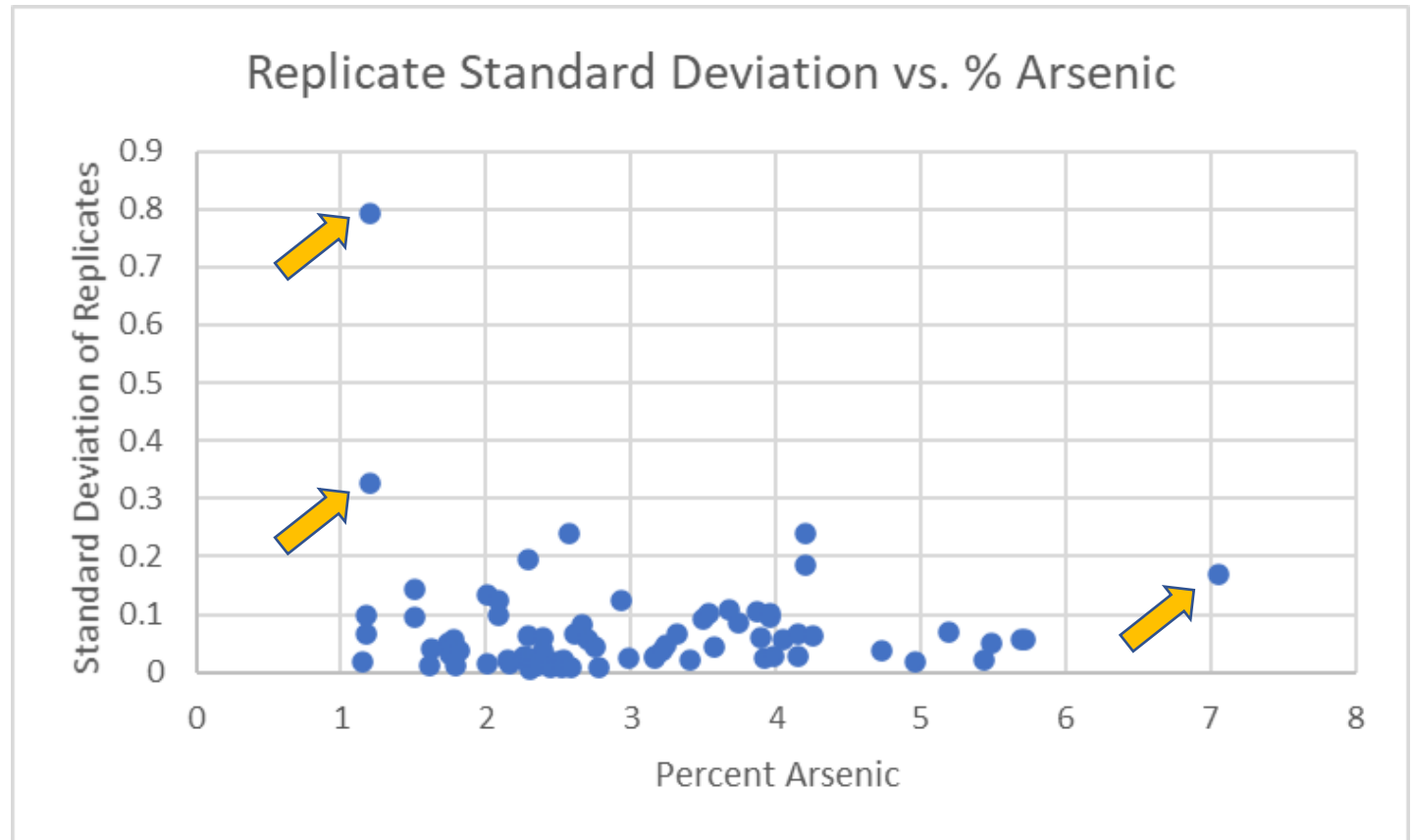
# Nickel/Silver induced variance:

Not dis-similar to the increased gold replicate Standard Deviation previously shown with increasing nickel silver content.



# Arsenic induced variance:

Unlike with the nickel silver gold alloy, once the arsenic content exceeded a threshold of about 1% the standard deviation was not correlated with the increase in arsenic content up to at least 7% arsenic in the sample.



# Comparison of Two Mine Feeds

- The 4-replicate standard deviation averaged to be 7 times higher for the high arsenic-lead material over the low arsenic-lead material.
- Typically tried to compensate by running more replicates.
- Often enough to virtually use the whole pin sample.
- Run reserve samples.



# Comparison of Two Mine Feeds

- With the high arsenic lead material:
  - The splitting limit is 0.10% or ~2.5 t oz of gold.
  - The laboratory ran repeats and additional samples 80% of the time.
  - 27% of lots ended up at umpire.
- Low arsenic lead material:
  - Same splitting limit.
  - No repeats or additional samples run.
  - 5% of lots went to umpire.

# Comparison of Two Mine Feeds

- With the high arsenic lead material:
  - Using the calculation cited previously the data would generate a splitting limit of 0.32%.
  - Umpires would be reduced by three quarters to 8%.
- Low arsenic lead material:
  - Using the calculation cited previously the data would generate a splitting limit of 0.064%.
  - Umpires would actually increase to 12% of exchanges.

# Comparison of Two Mine Feeds

- Should this then be considered the splitting limit for these two materials?
- It is a guideline:
  - Assumes that the two laboratories are using the same technique with # of replicates.
  - Assumes no bias in either laboratory.
- That's not realistic – remember we are repeating or running other samples in 80% of the high arsenic lead samples.

From Dr. Alessandro Ruffoni's paper "Uncertainty and Fineness Marking of Bars", LBMA 2015

In the need to keep the uncertainty under proper control, two kinds of contributions have to be distinguished:

- (1) the ones related to the statistical error

They cannot be avoided, but they can be controlled and reduced



- (2) the ones related to systematic errors

They can have a significant and critical influence on the quality of the product (in our case on the fineness to be marked on the bar).

It is necessary to identify them so that can be avoided.



# Comparison of Two Mine Feeds

Further evidence of this?

While both mine labs are excellent, Asahi's win ratio at umpire:

- 80% of the umpires for the material with high arsenic and lead.
- 86% of the umpires for the material with low arsenic and low lead.

# Comparison of Two Mine Feeds

- This suggests that the refiner's lab and the mine lab are not on an equal footing. For many good reasons:
  - The refiner typically has more resources.
  - The refiner's lab is typically more specialized.
  - The refiner has a long history from which to draw as to what is the process capability of the analytical technique.

# Comparison of Two Mine Feeds

- When looking at our calculations:
  - This means that it is unlikely that the standard deviation is the same for both data sets.
  - It also means that the number of replicates used is not the same in both data sets.

# Comparison of Two Mine Feeds

- The refiner cannot however rely on the umpire to keep the settlement assay on the right path.
- Remember that in the case of the high arsenic-lead material Asahi ran 80% of those lots with more replicates and reserve samples to present its best analytical number.
- We cannot have the same expectation of the customer or the umpire.



# Comparison of Two Mine Feeds

- Therefore, as stated by Dr. Ruffoni in his 2015 LBMA presentation:

Leaving apart the systematic errors possibly related to the work of the analytical laboratory, considered elsewhere, it is important to focus our attention onto the sampling.

# Comparison of Two Mine Feeds

Therefore, to both ensure fair value to the customer and to protect its own inventory, the Refiner needs to focus on producing samples that tighten this circle of results as much as possible for all three laboratories.



# Comparison of Two Mine Feeds

- Focus on sampling technique.
- Often easier said than done.
- Producing samples that are consistent in themselves and from sample to sample is the goal.
- But that can be quite challenging with some of these metals present.

# Using Significant Difference as a Guide

- The exchange process is there to protect both the refiner and the customer.
- It limits the impact of bias and helps both parties identify biases to correct them.
- It guards against gross errors.
- If splitting limits are too wide or too narrow that value can be lost.

# Using Significant Difference as a Guide

- Since attending the 2015 conference I have used this paper's technique several times:
- When presented with splitting limits by others which seem out of line with the material to be assayed and exchanged – beyond the “process capability” of the analytical techniques to be used.
- When I have very little data, particularly when I am not familiar with the sampling technique or the material.

# Conclusion

- Deleterious metals can have severe impacts on the determination of the content of a lot sent to a refiner for evaluation.
- Many metals contribute to increasing the potential for error in that determination.
- Previously nickel and iron were examined and in this case lead and arsenic were reviewed.

# Conclusion

- Using the Significant Difference technique you can check the reasonableness of a proposed splitting limit.
- It highlights the consideration of the analytical process capability given the nature of the material being evaluated.
- Consider other factors when reaching what that splitting limit should be – study the data and see what it can tell you.

# Thanks & Acknowledgements

- Thanks very much to the LBMA for organizing and hosting this conference & for allowing me to make this presentation.
- I would also like to thank all those who continue to produce informative presentations for this conference, from which over the years I have learned many practical lessons.