Oddo-Harkins rule of element abundances

To instructors

This is a simple exercise that is meant to introduce students to the concept of isotope ratios, simple counting statistics, intrinsic instrument bias, correlated errors, analytical precision, and analytical accuracy. Students can prepare the solutions or they can be prepared beforehand (which is what I do in this case).

The exercise handout

In this exercise several solutions containing Eu will be analyzed for the two isotopes $^{151}$Eu and $^{153}$Eu. These are the only two stable isotopes of Eu. These isotopes will be repeatedly analyzed by ICP-MS in six synthetic solutions having Eu concentrations of 0 (a blank), 0.001, 0.01, 0.1, 1, and 10 ppb by weight. In each case counting times will be 10 seconds per isotope and the raw data will be presented in counts per second. Each sample will be analyzed 20 times. The raw data that you will work with will have only been corrected for detector dead time.

Procedure

1. Take the raw data (counts per second) and arrange them on a spreadsheet into paired columns (151 and 153 isotopes) by concentration.
2. Calculate the average blank count rate for each of the two isotopes.
3. Subtract the $^{151}$Eu average blank value from all of the $^{151}$Eu data values, and do the same for the $^{153}$Eu data values.
4. For each of the 20 blank subtracted isotope pairs for each concentration, calculate the $^{151}$Eu/$^{153}$Eu isotope ratio.
5. For each concentration take the 20 isotope ratio values you just calculated and now calculate the average isotope ratio for each concentration.
6. For each concentration take the 20 isotope ratio values and calculate the standard deviation of the mean at the 95% confidence limit for each isotope and for the isotope ratios ("=2*STDEV(the 20 ratio values)").
7. For each solution calculate the relative deviation of the mean at the 95% confidence limit for each isotope and for the isotope ratios. To do this, simply divide the standard deviation value you just calculated by the average value. Express this value in percent of the mean value.
8. Put together a small table on a separate spreadsheet showing how the average isotope ratio and relative deviation changes with Eu concentration in the analyzed solution.
9. Put together another small table. For each of the 5 Eu solutions there should be 3 columns. The third column should have the average $^{152}$Eu/$^{153}$Eu isotope ratio. The second column should have the average ratio minus the value of twice the standard deviation of the mean calculated in item 6. The first column should have the average ratio plus twice the standard deviation of the mean calculated in item 6.
10. Make a “Stock” type high-low-close graph that is available in Excel. Each of the three column sets for each of the 5 solution concentrations will be represented as an average point with error bars (see below).
11. For each solution compare the isotope ratios derived by ICP-MS, considering the error bars, to the actual isotope ratio derived from isotope abundances in the CRC Handbook of Chemistry and Physics or from web resources. Put this value as a horizontal line on the graph made in item 10.
1. For each of the five Eu concentrations, calculate the average of the blank subtracted count rates.
2. Multiply these numbers by ten to give the total number of ions actually counted during the 10 seconds that data were accumulated for each isotope for each solution.
3. Pretend that these new values are one determination for each of the solutions. Calculate two times the square root of each of these numbers. This is the estimated error for the isotope determinations based on counting statistics alone at the 95% confidence limit (see Appendix 1).
4. For each solution calculate the $^{151}\text{Eu}/^{153}\text{Eu}$ isotope ratio. When calculating a ratio, propagated relative errors are additive. Add the two relative errors together for calculated for each isotope for each solution to get an estimate of the average isotope ratios determined from counting statistics alone.
5. Compare this estimated relative deviation for the isotope ratios based on counting statistics with the relative deviation of the ratios themselves as calculated previously. Which are worse?

**Correlated error**

For this part of the exercise, concentrate only on the 10 ppb solution blank subtracted data. Copy these to another spreadsheet.

1. Calculate the average of the blank subtracted count rate data for each isotope, and the relative
deviation (in percent) for the average for the 95% confidence interval.

2. Calculate the $^{151}\text{Eu}/^{153}\text{Eu}$ isotope ratios for each of the 20 determinations.

3. Calculate the average of the isotope ratios and the relative deviation (in percent) for the average for the 95% confidence level.

4. How can it be that the isotope ratios yield a better precision than the data from which the average ratio is derived? To answer this question, plot a graph of the $^{151}\text{Eu}$ raw data against the $^{153}\text{Eu}$ blank subtracted data on an X-Y graph. Put a regression line through this set of 20 points. Does this help you answer the question?

Graph of the raw data for the 20 analyses of the 10 ppb Eu solution. Axes are scaled intensities. Note that the paired count rate values define an elongate area, showing that the raw data errors are in part correlated.

**For the writeup, comment on the following:**

1. Is the precision of each isotope determination similar to that expected from counting statistics alone?
2. For which solution is the mean isotope ratio most precise?
3. Does isotope ratio precision depend on element concentration?
4. Does isotope ratio accuracy depend on element concentration?
5. Do the measured isotope ratios agree with the book values within the 95% confidence limits?
6. Can you explain the reasons for the differences in isotope ratio precision?
7. Explain why the isotope ratio relative deviations are better than the relative deviations for each isotope alone. That is, the ratios seem to be as precise or more precise than the isotope signal intensities the ratio is calculated from. On the face of it, this does not make sense. One would think that the ratio of two numbers with uncertainty would have larger uncertainty than each of the two numbers themselves.
Appendix 1

Lets say we analyzed isotopes in solution at three different concentrations, each yielding the following total counts at each mass:

<table>
<thead>
<tr>
<th></th>
<th>Solution 1</th>
<th>Solution 2</th>
<th>Solution 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Isotope 1</td>
<td>Isotope 2</td>
<td>Isotope 1</td>
</tr>
<tr>
<td>Total counts</td>
<td>100</td>
<td>200</td>
<td>10,000</td>
</tr>
<tr>
<td></td>
<td>10,000</td>
<td>20,000</td>
<td>1,000,000</td>
</tr>
<tr>
<td>Square root of the total counts (67% confidence limit)</td>
<td>10</td>
<td>14.1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1410</td>
<td>1000</td>
</tr>
<tr>
<td>2 times the square root (95% confidence limit)</td>
<td>20</td>
<td>28.2</td>
<td>200</td>
</tr>
<tr>
<td>Estimated relative deviation in the determined total counts for each isotope based on total counts alone</td>
<td>20%</td>
<td>14.1%</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>2820</td>
<td>2000</td>
</tr>
<tr>
<td>Isotope ratio (isotope 1/isotope 2)</td>
<td>0.5</td>
<td>0.50</td>
<td>0.500</td>
</tr>
<tr>
<td>Estimated relative deviation for the isotope ratios based on total counts alone.</td>
<td>34%</td>
<td>3.4%</td>
<td>0.34%</td>
</tr>
<tr>
<td>Or to put the isotope ratios and precisions another way:</td>
<td>0.5 ± 0.17</td>
<td>0.50 ± 0.017</td>
<td>0.500 ± 0.0017</td>
</tr>
</tbody>
</table>

This table shows two major points: First, as the total counts increases the analytical precision improves; second, as total counts increases by a factor of 100, analytical precision on the count rate improves by only a factor of 10 based on counting statistics alone. Since all analytical techniques have inherent instabilities of their own, which are in addition to the errors inherent with counting statistics, these instabilities always make the actual analytical precision worse than the precision only based on counting statistics.

Notes

Things needed for this lab

- High-purity HNO₃.
- 100 ml volumetric flasks for diluting.
- Pipettes.
- 1000 ppm Eu standard solution.
- Autosampler test tubes.

Instrumentation lab exercises
Pedagogy web page

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