

Standard Addition Example Problem

Let's start with an analogy. You have a magical paper bag that contains some M&Ms. The bag has no mass and you can not see into it. The only thing you can do is find the mass and add M&M's. If you can figure out a way to determine the number of M&M's, you win the contents of the bag (yum).

So you begin by finding the mass of the M&M's in the bag:

$$\text{Mass}_{\text{initial}} := 50 \cdot \text{gm}$$

Next you add 5 M&M's to the bag and find the new mass:

$$\text{MM}_{\text{added}} := 5$$

$$\text{Mass}_{\text{final}} := 55 \cdot \text{gm}$$

From this information, you can determine the mass of the 5 M&M's that you added:

$$\text{Mass}_{\text{added}} := \text{Mass}_{\text{final}} - \text{Mass}_{\text{initial}}$$

$$\text{Mass}_{\text{added}} = 5 \cdot \text{gm}$$

Since you know how many M&M's you added, you can determine the mass of each M&M

$$\text{Mass}_{\text{MM}} := \frac{\text{Mass}_{\text{added}}}{\text{MM}_{\text{added}}}$$

$$\text{Mass}_{\text{MM}} = 1 \cdot \text{gm}$$

Now you know the mass of a single M&M, so you can determine the number of M&M's initially in the bag from the initial mass.

$$\text{MM}_{\text{initial}} := \frac{\text{Mass}_{\text{initial}}}{\text{Mass}_{\text{MM}}}$$

$$\text{MM}_{\text{initial}} = 50$$

And now it is time to eat!!!

So, now let's take a look at a chemistry problem.

Suppose you are analyzing an sample of dirt to determine the concentration of lead contamination. You take the dirt sample back to the lab and extract the lead from the sample using nitric acid. Then you dilute the nitric acid solution and determine the lead in the solution using your new ICP-AE spectrometer (inductively coupled plasma-atomic emission). Now you are going to use standard addition to determine the concentration.

$$\text{Signal}_{\text{sample}} := 0.5879$$

This is the signal from the instrument display for your sample solution.

At this point all you have is a signal for the sample. Without a calibration, there is no way to determine the concentration of the sample. (Just like there is no way to determine the number of M&M's in the bag if you only know the mass.)

The trick here, just like with the M&M's, is to add a known amount. This is called a spike (or standard addition). The concept is the same, but the math is just a bit trickier because the instrument measures concentration (for the M&M's the mass was for the total amount).

$$\text{ppm} := 10^{-6}$$

This just defines ppm for Mathcad.

$$C_{\text{standard}} := 500 \cdot \text{ppm}$$

This is the concentration of the standard that is used for the spike.

$$V_{\text{standard}} := 0.1 \cdot \text{mL}$$

This is the volume of standard that is used for the spike.

From the concentration and the volume of the spike, we can calculate the amount of lead that is added in the spike.

$$\text{mass}_{\text{spike}} := C_{\text{standard}} \cdot V_{\text{standard}} \cdot \left(\frac{1 \cdot \text{gm}}{1 \cdot \text{mL}} \right)$$

Assume that the density of the solution is 1, to find the mass since ppm is: $\frac{\text{mass}_{\text{part}}}{\text{mass}_{\text{total}}} \cdot 10^6$

$$\text{mass}_{\text{spike}} = 5 \cdot 10^{-5} \cdot \text{gm}$$

Since ppm is defined as 10^{-6} , Mathcad handles the multiplication by 10^{-6} .

Now, knowing the mass of the spike it is possible to calculate the increase in the concentration of the sample.

$$V_{\text{total}} := 100.0 \cdot \text{mL}$$

This is the total volume of the "spiked sample". This is prepared by adding the 0.1 mL of the standard to a 100 mL volumetric flask. Then dilute this to the mark with the sample solution (the same one analyzed initially).

$$C_{\text{spiked}} := \frac{\text{mass}_{\text{spike}}}{V_{\text{total}} \left(\frac{1 \cdot \text{gm}}{1 \cdot \text{mL}} \right)}$$

The spiked (or added) concentration.

$$C_{\text{spiked}} = 5 \cdot 10^{-7}$$

This is the increase in the concentration of the unknown. (Just like the number of M&M's added).

$$C_{\text{spiked}} = 0.5 \cdot \text{ppm}$$

Now that we have prepared the "spiked sample", we can measure the signal

$$\text{Signal}_{\text{spiked}} := 0.7816$$

This is the signal from the instrument for the spiked sample.

The signal increased (by a known amount) because we added (a known amount) in the spike. Since we know the increase in the signal and the increase in the concentration, we can calculate the signal for a known concentration (like the mass of a single M&M)

The signal of the spike:

$$\text{Signal}_{\text{spike}} := \text{Signal}_{\text{spiked}} - \text{Signal}_{\text{sample}}$$

$$\text{Signal}_{\text{spike}} = 0.1937$$

The spiked concentration:

$$C_{\text{spiked}} = 0.5 \cdot \text{ppm}$$

The instrument response $\left(\frac{\text{signal}}{\text{concentration}} \right)$

$$\text{Response} := \frac{\text{Signal}_{\text{spike}}}{C_{\text{spiked}}}$$

$$\text{Response} = 0.3874 \cdot \text{ppm}^{-1}$$

So from the above, we determined the response of the instrument:

$$\text{Response} = 0.3874 \cdot \text{ppm}^{-1} \quad \text{This means that a concentration of 1 ppm will give a signal of 0.387}$$

Now, recall the signal of the original sample:

$$\text{Signal}_{\text{sample}} = 0.5879$$

This corresponds to a sample concentration of:

$$C_{\text{sample}} := \frac{\text{Signal}_{\text{sample}}}{\text{Response}}$$

$$C_{\text{sample}} = 1.517553 \cdot \text{ppm}$$

So, there you have it. The concentration of the sample. using standard addition.

However, there was one subtle assumption made above. Go back and see if you can find it.

The assumption is that the signal from the "spiked sample" is equal to the signal from the sample plus the signal from the spike. Or that:

$$\text{Signal}_{\text{spiked}} = \text{Signal}_{\text{sample}} + \text{Signal}_{\text{spike}}$$

However, the concentration of sample in the "spiked sample" is not the same as the concentration of the sample in the "unknown". Because the sample is slightly diluted by the volume of the spiking solution (0.1 mL in this example). We can take this into account several different ways.

One way is to "scale" the signal to calculate the signal for the sample that was diluted in the spiking step:

$$\text{Signal}_{\text{sample_adjusted}} := \text{Signal}_{\text{sample}} \cdot \left(\frac{V_{\text{total}} - V_{\text{standard}}}{V_{\text{total}}} \right)$$

$$\text{Signal}_{\text{sample_adjusted}} = 0.587312 \quad \text{Notice that this correction has a very small effect. Recall that}$$

$$\text{Signal}_{\text{sample}} = 0.5879$$

Now repeat the above calculations using the adjusted signal from the sample.

The signal of the spike:

$$\text{Signal}_{\text{spike_adjusted}} := \text{Signal}_{\text{spiked}} - \text{Signal}_{\text{sample_adjusted}}$$

$$\text{Signal}_{\text{spike_adjusted}} = 0.194288$$

The response

$$\text{Response_adjusted} := \frac{\text{Signal}_{\text{spike_adjusted}}}{C_{\text{spiked}}}$$

$$\text{Response_adjusted} = 0.388576 \cdot \text{ppm}^{-1}$$

For comparison, the previous value was:

$$\text{Response} = 0.3874 \cdot \text{ppm}^{-1}$$

The adjusted response corresponds to a sample concentration of:

$$C_{\text{sample_true}} := \frac{\text{Signal}_{\text{sample}}}{\text{Response_adjusted}}$$

$$C_{\text{sample_true}} = 1.512961 \cdot \text{ppm}$$

For comparison, the previously calculated value was:

$$C_{\text{sample}} = 1.517553 \cdot \text{ppm}$$

The error introduced by the "assumption" made above is:

$$\frac{|C_{\text{sample_true}} - C_{\text{sample}}|}{C_{\text{sample_true}}} = 0.303511 \cdot \%$$

Now that everything is "figured out", let's work through it again backwards to see how it all checks out (and to see if it really makes sense).

We "know" that:

$$C_{\text{standard}} = 500 \cdot \text{ppm}$$

$$V_{\text{standard}} = 0.1 \cdot \text{mL}$$

$$V_{\text{total}} = 100 \cdot \text{mL}$$

$$\text{Response}_{\text{adjusted}} = 0.388576 \cdot \text{ppm}^{-1}$$

$$C_{\text{sample}_{\text{true}}} = 1.512961 \cdot \text{ppm}$$

Based upon this the "calculated" signal for the sample (If we did everything correctly here) would be:

$$\text{Signal}_{\text{calculated}} := C_{\text{sample}_{\text{true}}} \cdot \text{Response}_{\text{adjusted}}$$

$$\text{Signal}_{\text{calculated}} = 0.5879$$

$$\text{Signal}_{\text{sample}} = 0.5879$$

So the "calculated" signal is identical to the measured experimental signal for the sample.

And just for the exercise, let's figure out the spiked sample.

The mass of lead added from the spike:

$$\text{mass}_{\text{spike}} := C_{\text{standard}} \cdot V_{\text{standard}} \cdot \left(\frac{1 \cdot \text{gm}}{1 \cdot \text{mL}} \right)$$

$$\text{mass}_{\text{spike}} = 5 \cdot 10^{-5} \cdot \text{gm}$$

The mass of lead added from the unknown:

$$\text{mass}_{\text{sample}} := C_{\text{sample_true}} \cdot (V_{\text{total}} - V_{\text{standard}}) \cdot \left(\frac{1 \cdot \text{gm}}{1 \cdot \text{mL}} \right)$$

$$\text{mass}_{\text{sample}} = 1.511448 \cdot 10^{-4} \cdot \text{gm}$$

The total mass of lead

$$\text{mass}_{\text{spiked}} := \text{mass}_{\text{spike}} + \text{mass}_{\text{sample}}$$

The concentration of lead in the spiked sample

$$C_{\text{spiked_calculated}} := \frac{\text{mass}_{\text{spiked}}}{V_{\text{total}} \cdot \left(\frac{1 \cdot \text{gm}}{1 \cdot \text{mL}} \right)}$$

$$C_{\text{spiked_calculated}} = 2.011448 \cdot \text{ppm}$$

Which would give a signal of:

$$\text{Signal}_{\text{spiked_calculated}} := C_{\text{spiked_calculated}} \cdot \text{Response_adjusted}$$

$$\text{Signal}_{\text{spiked_calculated}} = 0.7816$$

$$\text{Signal}_{\text{spiked}} = 0.7816$$

So everything checks out.

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