

A very simple multivariate calibration [Lesson 4 of matrix algebra (matrix inversion)]

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So far our lessons in matrix algebra have covered matrix addition, subtraction and multiplication. Why not matrix division? Well the answer is that while you may divide a matrix by a scalar (i.e. a single variable) you cannot divide a matrix by another matrix. The solution is to remember that an alternative method for doing scalar division is to calculate the reciprocal of the denominator and then multiply it by the numerator. If we could calculate the inverse of a matrix then we would be able to do matrix division by a similar method. With some limitations this can be done; the most important limitation being that the matrix must be square. The arithmetic required for inverting a matrix is relatively simple for a 2×2 matrix but it soon becomes quite heavy. Happily for us there are efficient algorithms available which allow modern personal computers to invert even large matrices in seconds. The formula for a 2×2 matrix, \mathbf{B} , can be written as:

$$\text{if } \mathbf{B} = \begin{bmatrix} b_{1,1} & b_{1,2} \\ b_{2,1} & b_{2,2} \end{bmatrix}$$

then $\mathbf{B}^{-1} =$

$$\begin{bmatrix} b_{2,2}/(b_{1,1} \times b_{2,2} - b_{1,2} \times b_{2,1}) & -b_{1,2}/(b_{1,1} \times b_{2,2} - b_{1,2} \times b_{2,1}) \\ -b_{2,1}/(b_{1,1} \times b_{2,2} - b_{1,2} \times b_{2,1}) & b_{1,1}/(b_{1,1} \times b_{2,2} - b_{1,2} \times b_{2,1}) \end{bmatrix}$$

where \mathbf{B}^{-1} is the inverse of \mathbf{B} .

It is obvious that the quantity $(b_{1,1} \times b_{2,2} - b_{1,2} \times b_{2,1})$ must not be equal to 0. Matrices with $(b_{1,1} \times b_{2,2} - b_{1,2} \times b_{2,1}) = 0$ cannot be inverted.

An example:

$$\text{if } \mathbf{B} = \begin{bmatrix} 4 & 3 \\ 2 & 1 \end{bmatrix}$$

$$\begin{aligned} \text{then } \mathbf{B}^{-1} &= \begin{bmatrix} 1/(4 \times 1 - 3 \times 2) & -3/(4 \times 1 - 3 \times 2) \\ -2/(4 \times 1 - 3 \times 2) & 4/(4 \times 1 - 3 \times 2) \end{bmatrix} \\ &= \begin{bmatrix} 1/(-2) & -3/(-2) \\ -2/(-2) & 4/(-2) \end{bmatrix} = \begin{bmatrix} -0.5 & 1.5 \\ 1 & -2 \end{bmatrix} \end{aligned}$$

These formulae can be deduced from the specification that, in the same way that $k \times 1/k = 1$, $\mathbf{B} \times \mathbf{B}^{-1} = \mathbf{I}$ where \mathbf{I} is the identity matrix having values of 1 on its principal diagonal and 0 elsewhere, i.e.

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

for a 2×2 matrix.

(Normally a multiplication sign is not written in matrix algebra and we will not include them in the remainder of the article.) However, note that MATLAB does require a \star multiplication symbol. Thus the inverse of \mathbf{B} is the matrix \mathbf{X} which satisfies the equations:

$$\mathbf{XB} = \mathbf{I} \quad (\text{and } \mathbf{BX} = \mathbf{I})$$

$$\text{if } \mathbf{X} = \begin{bmatrix} w & x \\ y & z \end{bmatrix} \text{ and } \mathbf{B} = \begin{bmatrix} a & b \\ c & d \end{bmatrix}$$

$$\text{and } \mathbf{BX} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

from our knowledge from Lesson 3¹ we can expand \mathbf{BX} :

$$\mathbf{BX} = \begin{bmatrix} wa + xc & wb + xd \\ ya + zc & yb + zd \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

i.e.

$$wa + xc = 1 \tag{1}$$

$$wb + xd = 0 \tag{2}$$

if we multiply Equation (1) by d and Equation (2) by c then we have:

$$wad + xcd = d \tag{3}$$

$$wbc + xdc = 0 \tag{4}$$

now subtract (4) from (3):

$$w(ad - bc) = d$$

$$w = d/(ad - bc)$$

if we substitute for w in Equation (2) we have:

$$db/(ad - bc) + xd = 0$$

$$xd = -db/(ad - bc)$$

$$x = -b/(ad - bc)$$

Similarly

$$ya + zc = 0$$

$$yb + zd = 1$$

$$yad + zcd = 0$$

$$ybc + zdc = c$$

$$y(ad - bc) = -c$$

$$y = -c / (ad - bc)$$

$$yb + zd = 1$$

$$-cb / (ad - bc) + zd = 1$$

$$zd = 1 + cb / (ad - bc)$$

$$zd = (ad - bc + cb) / (ad - bc)$$

$$z = a / (ad - bc)$$

A demonstration of matrix inversion

We are going to demonstrate the use of matrix inversion to solve a pair of simultaneous equations which is in the form of the most simple multivariate calibration having just two variables and two components, (a 2×2 matrix).

This is historically important data because it has been used by Harald Martens to explain multivariate calibrations for at least 15 years but we acquired it from the www.wiley.co.uk/chemometrics website where it is associated with the new book by Harald and Magni Martens.²

The data is a small set of spectra of litmus solutions made from various dilutions of an original litmus solution and at varying pH. The spectra were measured at 8 nm intervals from 416 to 792 nm and they are shown in Figure 1. Apart from one neutral solution the others are either acidic (red) or alkaline (blue). The problem is to be able to determine the amount of litmus present irrespective of the pH.

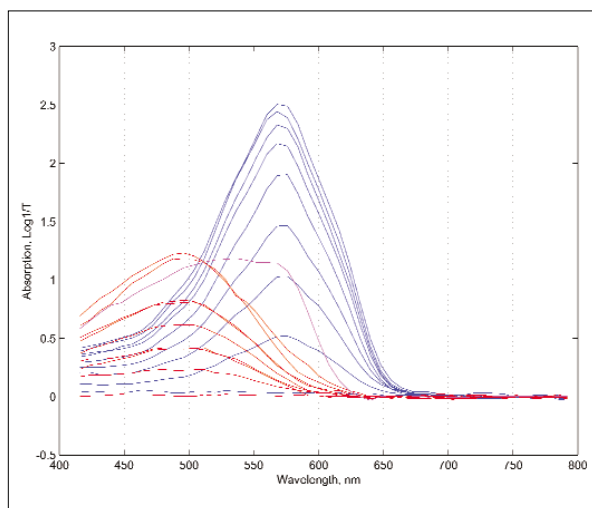


Figure 1. Spectra of 19 litmus solutions from Reference 2.

If all solutions were either acidic or alkaline then we would be able to write a Beer's law equation:

$$a = bcd$$

where a is the absorption, b the absorption coefficient, c is the concentration of the analyte and d the cell dimension; and a ,

b , c , d have no connection to the previous arbitrary use of these letters. For a unit length cell this can be re-written in terms of concentration:

$$c = a/b$$

and this could be solved using the absorption at one wavelength.

If we have two absorbing species then we need measurements at least two wavelengths:

$$a_1 = b_{1,1} \times c_1 + b_{1,2} \times c_2$$

$$a_2 = b_{2,1} \times c_1 + b_{2,2} \times c_2$$

where a_1 , a_2 are the absorptions at wavelengths 1 and 2; $b_{1,1}$ is the absorption coefficient for the first species at the first wavelength, $b_{2,1}$ is the absorption coefficient for the first species at the second wavelength, $b_{2,2}$ is the absorption coefficient for the second species at the second wavelength, and c_1 and c_2 are the concentrations of the first and second species.

The matrix form of this expression is:

$$\mathbf{a} = \mathbf{B}\mathbf{c}$$

which has the solution:

$$\mathbf{c} = \mathbf{B}^{-1}\mathbf{a}$$

Given absorption values at two wavelengths for one sample, and the matrix \mathbf{B} of absorption coefficients, we could use the above equation to estimate the concentrations of the two species for that sample. Given 19 such samples we could do 19 separate and very similar calculations. However, it is more efficient (and more fun) to do what MATLAB users call "vectorising" the equations. Notice that all of them involve exactly the same \mathbf{B} matrix, so if we put the 19×2 column vectors of absorptions side by side to make a 2×19 matrix \mathbf{A} , and put all the (unknown) concentrations side by side to make another 2×19 matrix \mathbf{C} , we can write all 19 equations at once as

$$\mathbf{A} = \mathbf{B}\mathbf{C}$$

which has the solution:

$$\mathbf{C} = \mathbf{B}^{-1}\mathbf{A} \quad (5)$$

Our data has measurements at 48 wavelengths and so we will calculate absorption coefficients at every wavelength using both the nine blue samples and the nine red samples. Then we will chose likely wavelengths to put into Equation 5.

Here is the MATLAB program with instructions in red and program comments in green.

```
% LitmusB
% Demonstrates inversion of B coefficients
% Data from Harald Martens
load litmus2
a=S_V(:,2:49); % the absorption data
c=S_V(:,1); % the litmus concentration data
w=[416:8:792]; % wavelength range
% these are the blue ones
cb=c(1:9);
ab=a(1:9,:);
% these are the red ones
cr=c([10:16 18 19]);
ar=a([10:16 18 19],:);
% this is the purple one
cp=c(17);
ap=a(17,:);
% Look at the data
```

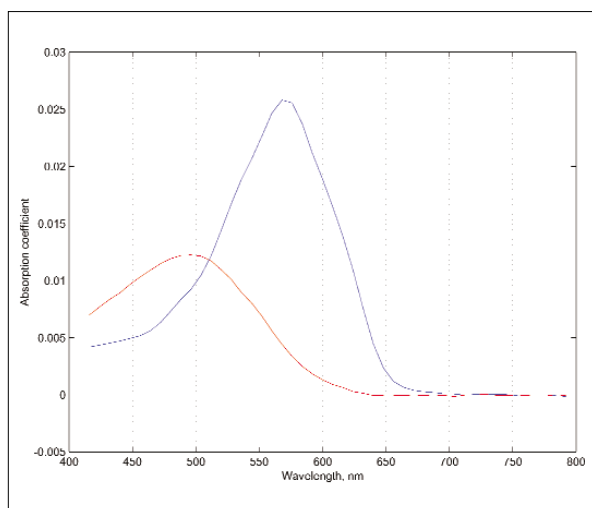


Figure 2. Variation of absorption coefficients with wavelength for the red and blue forms of litmus.

```
figure
plot(w,ab','b')
hold on
plot(w,ar','r')
plot(w,ap','m')
xlabel('Wavelength, nm')
ylabel('Absorption, Log1/T')
hold off
pause
% Estimate absorption coefficients by a least
% squares regression
% THIS WILL BE EXPLAINED ON ANOTHER OCCASION
bcoefb=cb'*ab/(cb'*cb);
bcoefr=cr'*ar/(cr'*cr);

This might look like a matrix division but cb and cr are
9 x 1 so cb' + cb is a scalar
% bcoef is 48 * 2, has coeffs by wavelength
% for blue in col 1,
% red in col 2, estimated by regression
% through the origin
bcoef=[bcoefb' bcoefr'];
%look at coeffs
figure % this is Figure 2
plot(w,bcoefb)
hold on
plot(w,bcoefr,'r')
xlabel('Wavelength, nm')
ylabel('Absorption coefficient')
hold off
pause
% pick the wavelengths at the top of the peaks
% and try
w1=10; % 488 nm
ww1=416+(w1-1)*8
w2=20; % 568 nm
ww2=416+(w2-1)*8
% B is 2 x 2, with row 1 having the coeffs for
% blue, red
% at wavelength w1, row 2 at wavelength w2
B=bcoef([w1 w2],:);
```

Table 1. Results for the prediction of litmus components using absorption data at 488 and 568 nm.

% Litmus	Blue components	Red components	Total	Error	Comment
100	94.2	2.9	97.0	3.0	
100	96.2	4.9	101.1	-1.1	
93	90.5	-1.3	89.1	3.9	
83.5	84.2	-1.0	83.2	0.3	
67	74.3	-4.9	69.3	-2.3	
50	57.2	-3.4	53.8	-3.8	
33	40.1	-1.8	38.3	-5.3	
16.5	20.1	-0.7	19.4	-2.9	
0	0.8	1.9	2.8	-2.8	
0	0.1	0.4	0.6	-0.6	
16.5	0.2	18.4	18.5	-2.0	
33	-0.5	34.8	34.3	-1.3	
33	-0.7	34.0	33.3	-0.3	
50	-1.0	50.9	49.9	0.1	
67	-0.5	65.7	65.3	1.7	
67	-1.3	67.7	66.4	0.6	
95	33.4	63.9	97.3	-2.3	Purple
97	3.3	94.7	98.0	-1.0	
100	-1.2	100.9	99.7	0.3	

```
% A is 2 x 19, it has the absorbancies at the
% two wavelengths
% for all 19 samples
A=a(:,[w1 w2])';
% solve the equation BC=A
% NOW WE DO THE INVERSION!!
C=inv(B)*A;

This simple instruction actually solves 19 sets of simultane-
ous equations at once!
% C has est blue, red in cols 1,2
% it isn't bad!
s=sum(C)';
e=c-s;
[c C' s e]; % this prints the results
%Actual, est blue, est red, total, error
```

The results are given in Table 1. These results are reasonable considering the assumption that the absorptions are linear over the concentration range. Although there are some quite large errors it is pleasing to see that the purple sample is estimated reasonably satisfactorily even though it could not be used in the estimation of the absorption coefficients.

In our next lesson we will consider how this data could be used more effectively, while learning more about the intricacies of matrix algebra.

References

1. A.M.C. Davies and T. Fearn, *Spectroscopy Europe* **12**(6), 22 (2000).
2. H. Martens and M. Martens, *Multivariate Analysis of Quality: An Introduction*. Wiley, Chichester (2001).