AUTOMATIC EVALUATION AND DATA GENERATION FOR ANALYTICAL CHEMISTRY INSTRUMENTAL ANALYSIS EXERCISES

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Exercise 1

A new analytical method for the determination of molybdenum by molecular luminescence has been developed. The calibration curve is established by an external standard calibration method employing five standards by triplicate. This method is then used to analyze an unknown sample, also by triplicate.

The experimental data of the exercise is personalized for each student. To obtain the data, download the file exercise1_data.p from the course web. This file is a program that has to be executed in Matlab's workspace invoking its name and that given the ID number generates a –html file with the data.

For example, for the ID 80071067 the script generates the file 80071067.html with the following data:

```
EXERCISE DATA
ID 80071067

The three measures for the standard 1 (x = 0.2) are:
y1 = 4.25154, y2 = 3.93557, y3 = 4.30114

The three measures for the standard 2 (x = 0.4) are:
y1 = 4.2702, y2 = 4.21205, y3 = 4.25277

The three measures for the standard 3 (x = 0.8) are:
y1 = 4.73237, y2 = 4.96964, y3 = 4.78168

The three measures for the standard 4 (x = 1.6) are:
y1 = 5.46605, y2 = 5.5696, y3 = 5.4491

The three measures for the standard 5 (x = 3.2) are:
y1 = 7.45906, y2 = 7.40427, y3 = 7.12714

The three measures of the sample are:
y1 = 4.91009, y2 = 4.89413, y3 = 5.01947
```

Using the personalized data:

1. Calculate the quality parameters of the method: linearity, analytical resolution (before known as analytical sensitivity), limit of detection according to the Long and Winefordner and to the Clayton et al. criteria. Use α=0.05 y β=0.05 to apply the Clayton et al. criterium.
2. What is the molybdenum concentration of the unknown sample? Express the result with the correct number of significant figures and with a confidence level of 95 %, indicating the accuracy.

The results of the exercise must be sent to the instructor using the Goodle server. The students must provide the linearity (lin), the analytical resolution (res), the limits of detection according to the Long and Winefordner (LODWL) and Clayton (LODC) criteria and, finally, the calculated concentration of the molybdenum in the problem sample (x_p), as well as the associated uncertainty (e_p). The students must provide the answer with a single uncertain digit. The results are submitted in text form with the following structure:

```
Quality_parameters = [lin res LODWL LODC];
Concentration = [xp ep];
```

For example, for the ID 80071067 the correct answer is:

```
Quality_parameters = [96.8269 0.1341 0.3826 0.3252];
Concentration = [0.9 0.2];
```

exercise1_data.p

```
DNI=input ('Input ID:');

% A deterministic seed based on the ID is provided
rand('seed',DNI);

% Random slope and bias of the method
dni_pdt = 1 + 4*rand(1);
dni_oor = 1 + 4*rand(1);

% Random data generated for the particular ID
% Each measurement has a 5% error

% Standard measures
Concentraciones=[0.2;0.4;0.8;1.6;3.2];
Abs_dni=[];
Absorbancias=[];
for j=1:5
    Abs=Concentraciones(j)*dni_pdt+dni_oor;
    erel = 0.05;
    for kk=1:3
        aux = (1-erel) + 2*erel*rand(1);
        Abs_dni=[Abs_dni (aux*Abs)];
    end
    Absorbancias=[Absorbancias;Abs_dni];
    Abs_dni=[];
end

% Sample measures
```

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```
replicas = [];
dni_xu = 0.5 + 2.5*rand(1);
repl=dni_xu*dni_pdt+dni_oor;
for k=1:3
    aux = 0.95 + 0.1*rand(1);
    replicas=[replicas aux*repl];
end

replicas=replicas';
Absorbancias;

disp(sprintf('File %d.html generated',DNI));

comentarios = '<html lang="es"> <body> EXERCISE DATA
<br>';
comentarios = strcat(comentarios,sprintf(' ID %d
<br><br>',DNI));
for i=1:5
    comentarios = strcat(comentarios,sprintf(' The
three measures for the standard %d (x = %g) are:<br>'
,i,Concentraciones(i)));
    comentarios = strcat(comentarios,sprintf(' y1 =
%g, y2 = %g, y3 = %g<br><br>',Absorbancias(i,1),Absor
bancias(i,2),Absorbancias(i,3)));
end
comentarios = strcat(comentarios,sprintf(' The three
measures of the sample are:<br>'));
comentarios = strcat(comentarios,sprintf(' y1 = %g,
y2 = %g, y3 = %g<br>',replicas(1),replicas(2),replic
as(3)));
comentarios = strcat(comentarios,'</body> </html>');
fid = fopen(sprintf('%d.html',DNI),'w');
fprintf(fid,'%s',comentarios);
fclose(fid);
```

exercise1_eval.m

```
% The ID is stored in variable dni in text form auto-
matically by GOODLE GMS
DNI = str2num(dni);

% A deterministic seed based on the ID is provided
rand('seed',DNI);

% Random slope and bias of the method
dni_pdt = 1 + 4*rand(1);
dni_oor = 1 + 4*rand(1);

% Random data generated for the particular ID
% Each measurement has a 5% error

% Standard measures
Concentraciones=[0.2;0.4;0.8;1.6;3.2];
Abs_dni=[];
Absorbancias=[];
for j=1:5
    Abs=Concentraciones(j)*dni_pdt+dni_oor;
    erel = 0.05;
    for kk=1:3
        aux = (1-erel) + 2*erel*rand(1);
        Abs_dni=[Abs_dni (aux*Abs)];
    end
    Absorbancias=[Absorbancias;Abs_dni];
    Abs_dni=[];
end

% Sample measures
replicas = [];
dni_xu = 0.5 + 2.5*rand(1);
repl=dni_xu*dni_pdt+dni_oor;
for k=1:3
    aux = 0.95 + 0.1*rand(1);
    replicas=[replicas aux*repl];
end

replicas=replicas';
Absorbancias;

patron=[Concentraciones,Absorbancias];

% First, the correct solution is computed
m=15;
ac_file=[];
for i=1:5
    for j=2:4
        ac_file=[ac_file;patron(i,1),patron(i,j)];
    end
end

ac_b=[cov(ac_file(:,1),ac_file(:,2))]/
[(std(ac_file(:,1)))^2];
ac_pdt=ac_b(2,1);
ac_oor=mean(ac_file(:,2))-ac_pdt*(mean(ac_file(:,1)));
ac_ycalajus=ac_oor+(ac_file(:,1)).*ac_pdt;
ac_sysobx=((sum((ac_file(:,2)-ac_ycalajus).^2))/
(m-2))^(1/2);
t=2.16;

% Calculated concentration of the molybdenum in the
problem sample (xp), as
% well as the associated uncertainty
ac_xu=(mean(replicas)-ac_oor)./ac_pdt;
ac_int_conf=t*((1/3+1/15+((mean(replicas)-
-mean(ac_file(:,2))).^2)./(ac_pdt^2*sum((ac_file(:,1)-
-mean(ac_file(:,1))).^2))).^(1/2)).*ac_sysobx/
ac_pdt;

% The results are rounded with a single uncertain
digit
e = 1;
while floor(e*ac_int_conf)<1
    e=10*e;
end
ep = round(e*ac_int_conf)/e;
xp = round(e*ac_xu)/e;

Resultado_concentracion_P=[xp ep];

% Quality parameters
% Lineality
Tsumxcuad=sum((ac_file(:,1)).^2);
Tmedxexp=mean((ac_file(:,1)));
Tdif=(ac_file(:,1)-Tmedxexp);
Tdifcuadx=Tdif.^2;
Tsumdifcuadx=sum(Tdifcuadx);
Tdesvord=((Tsumxcuad)/
```

```
(m*(Tsumdifcuadx)))^(1/2)*ac_sysobx;
Tdesvpdt=((1/sum((ac_file(:,1)-mean(ac_
file(:,1))).^2))^(1/2))*ac_sysobx;
L=(1-Tdesvpdt/ac_pdt)*100;

% Analytical resolution
S_a=ac_sysobx/ac_pdt;

% Limits of detection according to the Long and
Winefordner (LODWL) and
% Clayton (LODC) criteria
X_LOD_WL=(3*(0+Tdesvord^2+(ac_oor/
ac_pdt)^2*Tdesvpdt^2)^(1/2))/ac_pdt;
wo_2=1/3+1/15+(mean(ac_file(:,1)))^2*1/
sum((ac_file(:,1)-mean(ac_file(:,1))).^2);
delta= 3.4787;
X_LOD_CLAYTON=delta*(wo_2^(1/2))*ac_sysobx/ac_pdt;


% Correct solution
Resultados_parametros_calidad_P=[L,S_a,X_LOD_WL,X_
LOD_CLAYTON];

comentarios = '<html lang="es"> <body> RESULTS <br>';
comentarios = strcat(comentarios,sprintf(' ID %s
<br><br>',dni));

comentarios = strcat(comentarios,sprintf(' Calculated
concentration<br><br>'));
comentarios = strcat(comentarios,sprintf(' Results
(raw): %g ppm +-%g ppm <br>',ac_xu,ac_int_conf));
comentarios = strcat(comentarios,sprintf(' Results
(rounded):  %g ppm +-%g ppm <br>',xp,ep));
comentarios = strcat(comentarios,sprintf(' Results
(student): %g ppm +-%g ppm <br>',Concentracion(1),Con
centracion(2)));

comentarios = strcat(comentarios,sprintf('<br>
Correct quality parameters: <br><br>'));
comentarios = strcat(comentarios,sprintf('Lineality
(lin): %g <br>',Resultados_parametros_calidad_P(1)));
comentarios = strcat(comentarios,spri
ntf('Analytical resolution (res): %g
<br>',Resultados_parametros_calidad_P(2)));
comentarios = strcat(comentarios,sprintf('(LODWL): %g
<br>',Resultados_parametros_calidad_P(3)));
comentarios = strcat(comentarios,sprintf('(LODC): %g
<br>',Resultados_parametros_calidad_P(4)));

comentarios = strcat(comentarios,sprintf('<br>
Students quality parameters: <br><br>'));
comentarios = strcat(comentarios,sprintf('Lineality
(lin): %g <br>',Parametros_calidad(1)));
comentarios = strcat(comentarios,sprintf('Analytical
resolution (res): %g <br>',Parametros_calidad(2)));
comentarios = strcat(comentarios,sprintf('(LODWL): %g
<br>',Parametros_calidad(3)));
comentarios = strcat(comentarios,sprintf('(LODC): %g
<br>',Parametros_calidad(4)));

nota = 0;
if(abs(Concentracion(1)-ac_xu)<ac_int_conf)
    nota = nota + 2.5;
    comentarios = strcat(comentarios,sprintf('<br>The
concentration is correct (2.5) <br><br>'));
else
    comentarios = strcat(comentarios,sprintf('<br>The
concetration is not correct<br><br>'));
end

if(Concentracion(2)==ep)
    nota = nota +2.5;
    comentarios = strcat(comentarios,sprintf('The un-
certainty is correct (2.5) <br><br>'));
else
    comentarios = strcat(comentarios,sprintf('The un-
certainty is not correct<br><br>'));
end

k = 0;
for i=1:4
    if(abs(Resultados_parametros_calidad_P(i)-Para-
metros_calidad(i))<0.01*abs(Resultados_parametros_
calidad_P(i)))
        nota = nota+1.25;
        k = k+1;
    end
end
comentarios = strcat(comentarios,sprintf(' %d quality
parameters correct (1.25each)<br><br>',k));

comentarios = strcat(comentarios,sprintf('<br>Grade
%g <br>',nota));
comentarios = strcat(comentarios,'</body> </html>');
```

Exercise 2

The total iron content of a siliceous rock has been determined by two different analytical methods, methods A and B. Absorption atomic spectroscopy and molecular spectrophotometry have been employed as analytical techniques for methods A and B, respectively.

Determine if there are significant differences in the total iron content obtained using both methods with a confidence level of 95 %.

The experimental data of the exercise is personalized for each student. To obtain the data, download the file exercise2_data.p from the course web. This file is a program that has to be executed in Matlab's workspace invoking its name and that given the ID number generates a –html file with the data.

For example, for the ID 80071067 the script generates the file 80071067.html with the following data:

```
EXERCISE DATA
ID 80071067

Method A Atomic absorption spectroscopy
Fe2O3 (percentage)
36.8961
36.6263
36.1783
34.7433
35.8801

Method B Molecular spectroscopy
Fe2O3 (percentage)
36.1608
```

```
36.0275
36.1827
35.7914
35.8459
36.1211
36.2558
35.8745
35.8983
```

Using the personalized data:

1. The estimated $F_{calculated}$, $F_{tabulated}$, $T_{calculated}$, $T_{tabulated}$ values of the comparison test.
2. Indicate if there are statistically significative differences between the obtained results using the methods A and B.

The results of the exercise must be sent to the instructor using the Goodle server. The students must provide the Fcalculated (Fcal), Ftabulated (Ftab), Tcalculated (Tcal) and Ttabulated (Ttab) and that if there are or not significative differences (res). The parameter res must be 0 if there are not differences and 1 if there are differences. The students must provide the answer with a single uncertain digit. The results are submitted in text form with the following structure:

```
Test_parameters = [Fcal Ftab Tcal Ttab];
Results = res;
```

For example, for the ID 80071067 the correct answer is:

```
Test_parameters = [24.2764   5.0530   0.1249   4.3030];
Results = 0;
```

Exercise2_data.p

```
DNI=input ('Input ID:');

% A deterministic seed based on the ID is provided
rand(,seed',DNI);

t_distr=[1,12.706;
    2, 4.303;
    3, 3.182;
    4, 2.776;
    5, 2.571;
    6, 2.447;
    7, 2.365;
    8, 2.306;
    9, 2.262;
    10, 2.228;
    11, 2.201;
    12, 2.179;
    13, 2.160;
    14, 2.145;
    15, 2.131;
    16, 2.120;
    17, 2.110;
    18, 2.101;
    19, 2.093;
    20, 2.086;
    21, 2.080;
    22, 2.074;
    23, 2.069;
    24, 2.064;
    25, 2.060;
    26, 2.056;
    27, 2.052;
    28, 2.048;
    29, 2.045];

test_f5_doble=[647.8, 799.5, 864.2, 899.6, 921.8,
937.1, 948.2, 956.7, 963.3, 968.6;
    38.51, 39.00, 39.17, 39.25, 39.30, 39.33, 39.36,
39.37, 39.39, 39.40;
    17.44, 16.04, 15.44, 15.10, 14.88, 14.73, 14.62,
14.54, 14.47, 14.42;
    12.22, 10.65, 9.979, 9.605, 9.364, 9.197, 9.074,
8.980, 8.905, 8.844;
    10.01, 8.434, 7.764, 7.388, 7.146, 6.978, 6.853,
6.757, 6.681, 6.619;
    8.813, 7.26, 6.599, 6.227, 5.988, 5.820, 5.695,
5.600, 5.523, 5.461;
    8.073, 6.542, 5.890, 5.523, 5.285, 5.119, 4.995,
4.899, 4.823, 4.761;
    7.571, 6.059, 5.416, 5.053, 4.817, 4.652, 4.529,
4.433, 4.357, 4.295;
    7.209, 5.715, 5.078, 4.718, 4.484, 4.320, 4.197,
4.102, 4.026, 3.964;
    6.937, 5.456, 4.826, 4.468, 4.236, 4.072, 3.950,
3.855, 3.779, 3.717];

N = [5 10]; %Minimum and maximum number of samples
X = [10 90]; %Minimum and maximum value of the conce-
tration of the sample

% Randomly determine one of the four different cases
if rand(1)<0.5
    % Both methods have the same mean
    erelx = 0;
else
    % The means differ 5%
    if rand(1)<0.5
        erelx = 0.05;
    else
        erelx = -0.05;
    end
end
if rand(1)<0.5
    % Both methods have a similar variance
    % Maximum measurement errors of 2%
    erela = 0.02;
    erelb = 0.02;
else
    % There are significative differences in the
variance
    % Maximum measurement errors of 1% and 4%
    if rand(1)<0.5
        erela = 0.01;
        erelb = 0.04;
    else
        erela = 0.04;
        erelb = 0.01;
    end
end

% Determine the number of samples and the problem
concentration
na = N(1)+round((N(2)-N(1))*rand(1));
```

```
nb = N(1)+round((N(2)-N(1))*rand(1));
xa = X(1)+round((X(2)-X(1))*rand(1));
xb = (1+erelx)*xa;

% Generate the measurements
metodo_a = [];
for i = 1:na
    e = 2*(0.5-rand(1))*erela*xa;
    metodo_a(i) = xa + e;
end

metodo_b = [];
for i = 1:nb
    e = 2*(0.5-rand(1))*erelb*xb;
    metodo_b(i) = xb + e;
end

disp(sprintf('File %d.html generated',DNI));

comentarios = '<html lang="es"> <body> EXERCISE DATA
<br>';
comentarios = strcat(comentarios,sprintf(' ID %d
<br>',DNI));
comentarios = strcat(comentarios,sprintf('<br>Me
thod A Atomic absorption spectroscopy <br> Fe2O3
(percentage)<br>'));
for i=1:na
    comentarios = strcat(comentarios,sprintf('%g
<br>',metodo_a(i)));
end
comentarios = strcat(comentarios,sprintf('<b
r>Method B Molecular spectroscopy <br> Fe2O3
(percentage)<br>'));
for i=1:nb
    comentarios = strcat(comentarios,sprintf('%g
<br>',metodo_b(i)));
end
comentarios = strcat(comentarios,'</body> </html>');
fid = fopen(sprintf('%d.html',DNI),'w');
fprintf(fid,'%s',comentarios);
fclose(fid);
```

exercise2_eval.m

```
% The ID is stored in variable dni is text form auto-
matically by GOODLE GMS
DNI = str2num(dni);

% A deterministic seed based on the ID is provided
rand(,seed',DNI);

t_distr=[1,12.706;
    2, 4.303;
    3, 3.182;
    4, 2.776;
    5, 2.571;
    6, 2.447;
    7, 2.365;
    8, 2.306;
    9, 2.262;
    10, 2.228;
    11, 2.201;
    12, 2.179;
    13, 2.160;
    14, 2.145;
    15, 2.131;
    16, 2.120;
    17, 2.110;
    18, 2.101;
    19, 2.093;
    20, 2.086;
    21, 2.080;
    22, 2.074;
    23, 2.069;
    24, 2.064;
    25, 2.060;
    26, 2.056;
    27, 2.052;
    28, 2.048;
    29, 2.045];

test_f5_doble=[647.8, 799.5, 864.2, 899.6, 921.8,
937.1, 948.2, 956.7, 963.3, 968.6;
    38.51, 39.00, 39.17, 39.25, 39.30, 39.33, 39.36,
39.37, 39.39, 39.40;
    17.44, 16.04, 15.44, 15.10, 14.88, 14.73, 14.62,
14.54, 14.47, 14.42;
    12.22, 10.65, 9.979, 9.605, 9.364, 9.197, 9.074,
8.980, 8.905, 8.844;
    10.01, 8.434, 7.764, 7.388, 7.146, 6.978, 6.853,
6.757, 6.681, 6.619;
    8.813, 7.26, 6.599, 6.227, 5.988, 5.820, 5.695,
5.600, 5.523, 5.461;
    8.073, 6.542, 5.890, 5.523, 5.285, 5.119, 4.995,
4.899, 4.823, 4.761;
    7.571, 6.059, 5.416, 5.053, 4.817, 4.652, 4.529,
4.433, 4.357, 4.295;
    7.209, 5.715, 5.078, 4.718, 4.484, 4.320, 4.197,
4.102, 4.026, 3.964;
    6.937, 5.456, 4.826, 4.468, 4.236, 4.072, 3.950,
3.855, 3.779, 3.717];

N = [5 10]; %Minimum and maximum number of samples
X = [10 90]; %Minimum and maximum value of the conce-
tration of the sample

% Randomly determine one of the four different cases
if rand(1)<0.5
    % Both methods have the same mean
    erelx = 0;
else
    % The means differ 5%
    if rand(1)<0.5
        erelx = 0.05;
    else
        erelx = -0.05;
    end
end
if rand(1)<0.5
    % Both methods have a similar variance
    % Maximum measurement errors of 2%
    erela = 0.02;
    erelb = 0.02;
else
    % There are significative differences in the
variance
```

```
    % Maximum measurement errors of 1% and 4%
    if rand(1)<0.5
        erela = 0.01;
        erelb = 0.04;
    else
        erela = 0.04;
        erelb = 0.01;
    end
end

% Determine the number of samples and the problem
concentration
na = N(1)+round((N(2)-N(1))*rand(1));
nb = N(1)+round((N(2)-N(1))*rand(1));
xa = X(1)+round((X(2)-X(1))*rand(1));
xb = (1+erelx)*xa;

% Generate the measurements
metodo_a = [];
for i = 1:na
    e = 2*(0.5-rand(1))*erela*xa;
    metodo_a(i) = xa + e;
end

metodo_b = [];
for i = 1:nb
    e = 2*(0.5-rand(1))*erelb*xb;
    metodo_b(i) = xb + e;
end

% Methods A and B are sorted depending on the
variance
if std(metodo_a)<std(metodo_b)
    x1 = mean(metodo_b);
    s1 = std(metodo_b);
    n1 = length(metodo_b);
    x2 = mean(metodo_a);
    s2 = std(metodo_a);
    n2 = length(metodo_a);
else
    x1 = mean(metodo_a);
    s1 = std(metodo_a);
    n1 = length(metodo_a);
    x2 = mean(metodo_b);
    s2 = std(metodo_b);
    n2 = length(metodo_b);
end

[x1 s1 n1;x2 s2 n2];

% the variances of the two methods are compared
through the "F-test" or
% "Fischer test".

Ftab=test_f5_doble(n2-1,n1-1);
Fcal=s1^2/s2^2;

% Fcal and Ftab are compared to determine the appro-
priate mean test

if Fcal < Ftab
    % There are not significative differences between
the variances of the
    % two sets of results
    % The commom variance is used in the test
    s_2 = ((n1-1)*s1^2+(n2-1)*s2^2)/(n1+n2-2);
    t_cal = abs(x1-x2)/sqrt(s_2*(1/n1+1/n2));
    t_tab=t_distr(n1+n2-2,2);
else
    % There are significative differences between the
variances of the
    % two sets of results
    % The t-test of Cochran is used
    t_cal = abs(x1-x2)/sqrt(s1^2/n1+s2^2/n2);
    gl = (s1^2/n1+s2^2/n2)^2/(((s1^2/n1)^2)/
(n1+1)+((s2^2/n2)^2)/(n2+1))-2;
    gl = round(gl);
    t_tab = t_distr(gl,2);
end

% Correct solution
[Fcal Ftab t_cal t_tab];

comentarios = '<html lang="es"> <body> RESULTS <br>';
comentarios = strcat(comentarios,sprintf(' ID %s
<br><br>',dni));

comentarios = strcat(comentarios,sprintf(' Correct
solution: <br>'));
comentarios = strcat(comentarios,sprintf(' Fcal = %g
<br>',Fcal));
comentarios = strcat(comentarios,sprintf(' Ftab = %g
<br>',Ftab));
comentarios = strcat(comentarios,sprintf(' Tcal = %g
<br>',t_cal));
comentarios = strcat(comentarios,sprintf(' Ttab = %g
<br>',t_tab));
if(t_cal<t_tab)
    comentarios = strcat(comentarios,sprintf(' There
are not significative differences <br>'));
else
    comentarios = strcat(comentarios,sprintf(' There
are significative differences <br>'));
end
comentarios = strcat(comentarios,sprintf('<br>
Evaluation criteria:<br>'));
comentarios = strcat(comentarios,sprintf('If the re-
sults and the parameters are correct the grade is 10
<br>'));
comentarios = strcat(comentarios,sprintf('Else the
grade is 0 <br>'));
comentarios = strcat(comentarios,sprintf('The maximum
error is 5 percent<br>'));
comentarios = strcat(comentarios,sprintf('<br>'));

nota = 10;
eps = 0.05;
if abs(Fcal-Test_parameters(1))>eps*Fcal
    comentarios = strcat(comentarios,sprintf('Fcal is
wrong<br>'));
    nota = 0;
end
if abs(Ftab-Test_parameters(2))>eps*Ftab
    comentarios = strcat(comentarios,sprintf('Ftab is
wrong<br>'));
    nota = 0;
```

```
end
if abs(t_cal-Test_parameters(3))>eps*t_cal
    comentarios = strcat(comentarios,sprintf('Tcal is
wrong<br>'));
    nota = 0;
end
if abs(t_tab-Test_parameters(4))>eps*t_tab
    comentarios = strcat(comentarios,sprintf('Ttab is
wrong<br>'));
    nota = 0;
end
if (Results == 0)&(t_cal>t_tab)
    comentarios = strcat(comentarios,sprintf('The re-
sults is wrong<br>'));
    nota = 0;
end
if (Results == 1)&(t_cal<t_tab)
    comentarios = strcat(comentarios,sprintf('The re-
sults is wrong<br>'));
    nota = 0;
end

comentarios = strcat(comentarios,sprintf('<br>Grade
%g <br>',nota));
```

Exercise 3

A new flame atomic absorption spectroscopy method for the determination of antimony in the atmosphere (method A) has been compared with the official spectroscopy method (method B). Determine if there are significant differences in the determination of antimony in the atmosphere using both methods with a confidence level of 95 %.

The experimental data of the exercise is personalized for each student. To obtain the data, download the file exercise3_data.p from the course web. This file is a program that has to be executed in Matlab's workspace invoking its name and that given the ID number generates a –html file with the data.

For example, for the ID 80071067 the script generates the file 80071067.html with the following data:

```
EXERCISE DATA
ID 80071067

Method A
New method
Antimony(mg/m3)
86.22
40.48
37.15
32.49
66.75
20.47
66.96
44.35
54.63

Method B
Standard method
Antimony(mg/m3)
83.62
45.05
39.77
37.11
72.21
22.84
68.59
47.45
52.51
```

Using the personalized data:

1. The estimate $T_{calculated}$ and $T_{tabulated}$ values of the comparison test.
2. Indicate if there are statistically significative differences between the obtained averages using the methods A and B.

The results of the exercise must be sent to the instructor using the Goodle server. The students must provide Tcalculated (Tcal) and Ttabulated (Ttab) and that if there are or not significant differences (res). The parameter res must be 0 if there are not differences and 1 if there are differences. The students must provide the answer with a single uncertain digit. The results are submitted in text form with the following structure:

```
Test_parameters = [Tcal Ttab];
Results = res;
```

For example, for the ID 80071067 the correct answer is:

```
Test_parameters = [2.2954   2.3060];
Results = 0;
```

exercise3_data.p

```
DNI=input ('Input ID:');

% A deterministic seed based on the ID is provided
rand(,seed',DNI);

t_distr=[1,12.706;
    2, 4.303;
    3, 3.182;
    4, 2.776;
    5, 2.571;
    6, 2.447;
    7, 2.365;
    8, 2.306;
    9, 2.262;
    10, 2.228;
    11, 2.201;
    12, 2.179;
    13, 2.160;
    14, 2.145;
    15, 2.131;
    16, 2.120;
    17, 2.110;
    18, 2.101;
    19, 2.093;
    20, 2.086;
    21, 2.080;
    22, 2.074;
    23, 2.069;
    24, 2.064;
    25, 2.060;
    26, 2.056;
    27, 2.052;
    28, 2.048;
```

```
    29, 2.045];

N = [5 10]; %Minimum and maximum number of samples
X = [10 90]; %Minimum and maximum value of the conce-
tration of the sample

% Randomly determine one of the two different cases
% Each case provides a different measurement error
for each method
if rand(1)<1
    erel1 = 0.2;
    erel2 = 0.1;
else
    erel1 = 0.01;
    erel2 = 0.01;
end

% Number of samples analized
n = N(1)+round((N(2)-N(1))*rand(1));

% Generate the measurements taking into account the
error of each method
dat_met_1 = [];
dat_met_2 = [];
for i = 1:n
    x = X(1)+round((X(2)-X(1))*rand(1));
    e1 = 2*(0.5-rand(1))*erel1*x;
    e2 = 2*(0.5-rand(1))*erel2*x;
    dat_met_1(i) = round(100*(x + e1))/100;
    dat_met_2(i) = round(100*(x + e1 + e2 + 3))/100;
end

disp(sprintf('File %d.html generated',DNI));

comentarios = '<html lang="es"> <body> EXERCISE DATA
<br>';
comentarios = strcat(comentarios,sprintf(' ID %d
<br>',DNI));
comentarios = strcat(comentarios,sprintf('<br>Method
A <br> New method<br>Antimony(mg/m3)<br>'));
for i=1:n
    comentarios = strcat(comentarios,sprintf('%g
<br>',dat_met_1(i)));
end
comentarios = strcat(comentarios,sprintf('<br>Method
B <br> Standard method<br>Antimony(mg/m3)<br>'));
for i=1:n
    comentarios = strcat(comentarios,sprintf('%g
<br>',dat_met_2(i)));
end
comentarios = strcat(comentarios,'</body> </html>');
fid = fopen(sprintf('%d.html',DNI),'w');
fprintf(fid,'%s',comentarios);
fclose(fid);
```

exercise3_eval.m

```
DNI = str2num(dni);
rand('seed',DNI);

t_distr=[1,12.706;
    2, 4.303;
    3, 3.182;
    4, 2.776;
    5, 2.571;
    6, 2.447;
    7, 2.365;
    8, 2.306;
    9, 2.262;
    10, 2.228;
    11, 2.201;
    12, 2.179;
    13, 2.160;
    14, 2.145;
    15, 2.131;
    16, 2.120;
    17, 2.110;
    18, 2.101;
    19, 2.093;
    20, 2.086;
    21, 2.080;
    22, 2.074;
    23, 2.069;
    24, 2.064;
    25, 2.060;
    26, 2.056;
    27, 2.052;
    28, 2.048;
    29, 2.045];

N = [5 10]; %Minimum and maximum number of samples
X = [10 90]; %Minimum and maximum value of the conce-
tration of the sample

% Randomly determine one of the two different cases
% Each case provides a different measurement error
for each method
if rand(1)<1
    erel1 = 0.2;
    erel2 = 0.1;
else
    erel1 = 0.01;
    erel2 = 0.01;
end

% Number of samples analized
n = N(1)+round((N(2)-N(1))*rand(1));

% Generate the measurements taking into account the
error of each method
dat_met_1 = [];
dat_met_2 = [];
for i = 1:n
    x = X(1)+round((X(2)-X(1))*rand(1));
    e1 = 2*(0.5-rand(1))*erel1*x;
    e2 = 2*(0.5-rand(1))*erel2*x;
    dat_met_1(i) = round(100*(x + e1))/100;
    dat_met_2(i) = round(100*(x + e1 + e2 + 3))/100;
end

d1=dat_met_1;
d2=dat_met_2;

% Calculate the mean of the differences
n=length(dat_met_1);
xd=[];
```

```
for i=1:n
    xd_i=((d1(1,i)-d2(1,i)));
    xd=[xd,xd_i];
    xd_i=[];
end
media=mean(xd);
% Calculate T_cal
t_cal=abs(mean(xd))/(std(xd)/sqrt(n));
% Calculate T_tab
t_tab=t_distr(n-1,2);

% Correct solution
[t_cal t_tab];

comentarios = '<html lang="es"> <body> RESULTS <br>';
comentarios = strcat(comentarios,sprintf(' ID %s
<br><br>',dni));

comentarios = strcat(comentarios,sprintf(' Correct
solution: <br>'));
comentarios = strcat(comentarios,sprintf(' Tcal = %g
<br>',t_cal));
comentarios = strcat(comentarios,sprintf(' Ttab = %g
<br>',t_tab));
if(t_cal<t_tab)
    comentarios = strcat(comentarios,sprintf(' There
are not significative differences <br>'));
else
    comentarios = strcat(comentarios,sprintf(' There
are significative differences <br>'));
end
comentarios = strcat(comentarios,sprintf('<br>
Evaluation criteria:<br>'));
comentarios = strcat(comentarios,sprintf('If the re-
sults and the parameters are correct the grade is 10
<br>'));
comentarios = strcat(comentarios,sprintf('Else the
grade is 0 <br>'));
comentarios = strcat(comentarios,sprintf('The maximum
error is 5 percent<br>'));
comentarios = strcat(comentarios,sprintf('<br>'));

nota = 10;
eps = 0.05;
if abs(t_cal-Parametros_test(1))>eps*t_cal
    comentarios = strcat(comentarios,sprintf('Tcal is
wrong<br>'));
    nota = 0;
end
if abs(t_tab-Parametros_test(2))>eps*t_tab
    comentarios = strcat(comentarios,sprintf('Ttab is
wrong<br>'));
    nota = 0;
end
if (Resultado == 0)&(t_cal>t_tab)
    comentarios = strcat(comentarios,sprintf('The re-
sult is wrong<br>'));
    nota = 0;
end
if (Resultado == 1)&(t_cal<t_tab)
    comentarios = strcat(comentarios,sprintf('The re-
sult is wrong<br>'));
    nota = 0;
end

comentarios = strcat(comentarios,sprintf('<br>Grade
%g <br>',nota));
```