FACULTY OF SCIENCE AND ENGINEERING

DEPARTMENT OF MATHEMATICS AND STATISTICS

REPEAT EXAMINATION PAPER 2013

MODULE CODE: MA4605 SEMESTER: Summer 2013

MODULE TITLE: Chemometrics DURATION OF EXAM: 2.5 hours

LECTURER: Mr. Kevin O'Brien GRADING SCHEME: 80 marks
70% of module grade

INSTRUCTIONS TO CANDIDATES

Scientific calculators approved by the University of Limerick can be used.
Formula sheet and statistical tables provided at the end of the exam paper.
Students must attempt any 4 questions from 5.

Question 1. (25 marks) Inference Procedures

- The nicotine content in blood can be determined by gas chromatography down to concentrations of 1 ng/ml. The concentration of nicotine was determined in each of two samples of known concentrations 10 ng/ml and 50 ng/ml.

```
Data: Sample (Lo): m = 10 ng/ml, n=14.

 8.40, 9.59, 9.38, 9.10, 10.78, 11.41, 9.94,
10.08, 12.11, 9.10, 9.59, 10.36, 10.41, 10.52.

Data: Sample (Hi): m = 50 ng/ml, n=10.

47.5, 48.4, 48.8, 48.4, 46.8,
46.2, 48.6, 50.6, 45.5, 46.1.
```

A research team evaluated both samples to determine whether or not the samples were similar in terms of measures of centrality and dispersion, before the trial commenced.

The following blocks of `R` code (i.e blocks 1 to 6) are based on the data for this assessment.

(a) (10 Marks) Each of the six blocks of code describes a statistical inference procedure. Provide a brief description for each procedure.

(b) (10 Marks) Write a short report on your conclusion for this assessment, clearly indicating which blocks of `R` code you felt were most relevant, and explain why.

Block 1

```
            F test to compare two variances

data:  Lo and Hi
F = 0.3945, num df = 13, denom df = 9, p-value = 0.1246
alternative hypothesis:
 true ratio of variances is not equal to 1
95 percent confidence interval:
 0.1029905 1.3066461
sample estimates:
ratio of variances
         0.3945149
```

Block 2

```
> shapiro.test(Lo)

        Shapiro-Wilk normality test

data:  Lo
W = 0.9779, p-value = 0.9609
> shapiro.test(Hi)

        Shapiro-Wilk normality test

data:  Hi
W = 0.9496, p-value = 0.6634
```

Block 3

```
> t.test(Lo,Hi)

        Welch Two Sample t-test

data:  Lo and Hi
t = -67.374, df = 14.016, p-value < 2.2e-16
alternative hypothesis:
   true difference in means is not equal to 0
95 percent confidence interval:
 -38.83294 -36.43706
sample estimates:
mean of x mean of y
   10.055    47.690
```

Block 4

```
> t.test(Lo,Hi,var.equal=TRUE)

        Two Sample t-test

data:  Lo and Hi
t = -72.6977, df = 22, p-value < 2.2e-16
alternative hypothesis:
   true difference in means is not equal to 0
95 percent confidence interval:
 -38.70863 -36.56137
sample estimates:
mean of x mean of y
   10.055    47.690
```

Block 5

```
> ks.test(Lo,Hi)

        Two-sample Kolmogorov-Smirnov test

data:  Lo and Hi
D = 1, p-value = 1.02e-06
alternative hypothesis: two-sided
```

Block 6

```
wilcox.test(Lo,Hi)

        Wilcoxon rank sum test


data:  Lo and Hi
W = 0, p-value = 1.02e-06
alternative hypothesis:
true location shift is not equal to 0
```

Question 2. (25 marks) Regression Models

(a) The fluorescence of each of a series of acidic solutions of quinine with concentrations 0,10,20,30,40,50 was determined five times. The mean values and standard deviations of these determinations have been obtained as follows:

Means:	4.0	21.2	44.6	61.8	78.0	105.2
Std Deviations:	0.71	0.84	0.89	1.64	2.24	3.03

Two models have been fitted to the data. These models are described by the following R code output.

Model 1
```
lm(formula = Means ~ Conc)

Coefficients:
Estimate Std. Error t value Pr(>|t|)
(Intercept) 2.9238 2.1648 1.351 0.248
Conc 1.9817 0.0715 27.715 1.01e-05 ***
---
Residual standard error: 2.991 on 4 degrees of freedom
Multiple R-squared: 0.9948,Adjusted R-squared: 0.9935
F-statistic: 768.1 on 1 and 4 DF, p-value: 1.008e-05
```

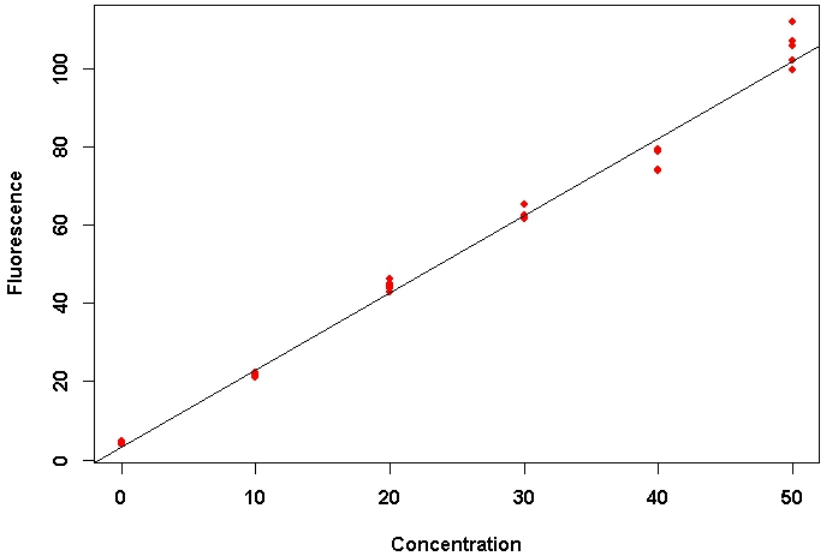
Model 2
```
weights=SdInt^(-2)/mean(SdInt^(-2))

lm(formula = Means ~ Conc, weights = weights)
Coefficients:
Estimate Std. Error t value Pr(>|t|)
(Intercept) 3.48066 1.15736 3.007 0.0397 *
Conc 1.96315 0.06765 29.018 8.4e-06 ***
---
Residual standard error: 2.034 on 4 degrees of freedom
Multiple R-squared: 0.9953,Adjusted R-squared: 0.9941
F-statistic: 842 on 1 and 4 DF, p-value: 8.396e-06
```

i. (4 Marks) What kind of analyses have been performed in each of model 1 and model 2? Write down the linear model regression equation fitted by each of the two analyses.

ii. (3 Marks) Describe differences between the two models, making reference to the scatter-plot of the data on the next page. (Also present on the scatter-plot is a regression line fitted using the first analysis).

iii. (2 Marks) Based on the R code output, which model is the better fit?



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(b) An ion-selective electrode (ISE) determination of sulphide from sulphate-reducing bacteria was compared with a gravimetric determination. Each pair of determinations were taken from the same sample.

The results obtained by both methods are expressed in milligrams of sulphide, and are tabulated below.

ISE method	108	12	152	3	106	11	128	12	160	128
gravimetry	105	16	113	1	108	11	141	161	182	118

Two simple linear models are fitted to the data. Model C uses the gravimetric determination as an independent variable used to predict the ISE determination. Conversely, Model D uses the ISE determination as an independent variable used to predict the gravimetric determination. The relevant `R` output is presented on the following page.

Model C

```
Call:
lm(formula = ISE ~ grav)
...
Coefficients:
            Estimate Std. Error t value Pr(>|t|)
(Intercept)  15.1125    28.8487   0.524    0.615
grav          0.6997     0.2543   2.751    0.025 *
....
```

Model D

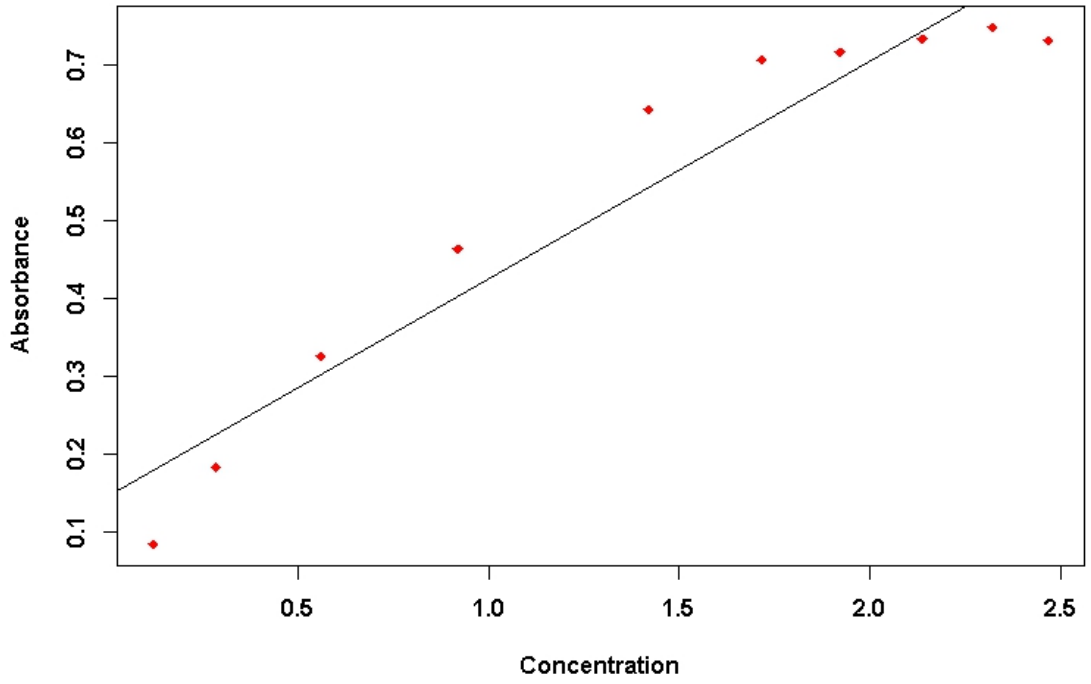
```
Call:
lm(formula = grav ~ ISE)
..
Coefficients:
            Estimate Std. Error t value Pr(>|t|)
(Intercept)  38.6215    25.8542   1.494    0.174
ISE           0.6949     0.2526   2.751    0.025 *
....
```

i. (3 marks) Is a simple linear regression model an suitable approach for this type of analysis? Explain why or why not? What alternative type of regression analysis might you recommend?

ii. (2 marks) Provide a brief description of the Bland-Altman plot. Discuss any shortcomings with this approach to method comparison.

(c) In an experiment to determine hydrolysable tannins in plants by absorption spectroscopy, the following results from ten samples were obtained and are tabulated below. A simple linear regression model, predicting absorbance values using concentration as the independent variable, was fitted to the data.

Sample	1	2	3	4	5
Absorbance	0.084	0.183	0.326	0.464	0.643
Concentration	0.123	0.288	0.562	0.921	1.420
Sample	6	7	8	9	10
Absorbance	0.707	0.717	0.734	0.749	0.732
Concentration	1.717	1.921	2.137	2.321	2.467



i. (1 marks) Is the simple linear regression model approach suitable for this study? Explain your answer with reference to the scatter-plot.

ii (3 marks) Two polynomial models were fitted to the data. Description of all three fitted models are found in the three blocks of `R` code below. The *Akaike information criterion* is listed, for each of the three fitted models. Write down the regression equations fo each ofthe three models.

iv. (2 marks) Specify which one of the models you would use. Justify your answer with appropriate statistical values.

Model 1

```
> summary(Model1)
Call:
lm(formula = Absorb ~ Conc)
...
Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept)    0.14412    0.04721   3.053   0.0158 *
Concentration  0.28088    0.02930   9.586 1.16e-05 ***
---
Signif. codes:  0 *** 0.001 ** 0.01 * 0.05 . 0.1   1

Residual standard error: 0.07584 on 8 degrees of freedom
Multiple R-squared: 0.9199,     Adjusted R-squared: 0.9099
F-statistic: 91.89 on 1 and 8 DF,  p-value: 1.163e-05
>
>AIC(Model1)
[1] -19.4343
```

Model 2

```
> summary(Model2)
Call:
lm(formula = Absorb ~ Conc + Conc.Squared)
...
Coefficients:
               Estimate Std. Error t value Pr(>|t|)
(Intercept)    0.006582   0.008013   0.821    0.439
Concentration  0.642935   0.015568  41.299 1.27e-09 ***
Conc.Squared  -0.140573   0.005894 -23.851 5.79e-08 ***
---
Signif. codes:  0 *** 0.001 ** 0.01 * 0.05 . 0.1   1

Residual standard error: 0.008939 on 7 degrees of freedom
Multiple R-squared: 0.999,      Adjusted R-squared: 0.9987
F-statistic:  3592 on 2 and 7 DF,  p-value: 2.879e-11
>
> AIC(Model2)
[1] -61.5338
```

Model 3 `> summary(Model3)`

```
Call:
lm(formula = Absorb ~ Conc+ Conc.Squared + Conc.Cubed)
...
...
Coefficients:
               Estimate Std. Error t value Pr(>|t|)
(Intercept)    0.013712   0.011629   1.179   0.2830
Concentration  0.608682   0.042825  14.213 7.58e-06 ***
Conc.Squared  -0.108186   0.038088  -2.840   0.0296 *
Conc.Cubed    -0.008196   0.009518  -0.861   0.4223
---
Signif. codes:  0 *** 0.001 ** 0.01 * 0.05 . 0.1   1

Residual standard error: 0.009109 on 6 degrees of freedom
Multiple R-squared: 0.9991,     Adjusted R-squared: 0.9987
F-statistic:  2306 on 3 and 6 DF,  p-value: 1.422e-09
>
> AIC(Model3)
[1] -60.69903
```

Question 3. (25 marks) Experimental Design

(a) Q5. In an investigation into the extraction of nitrate-nitrogen from air dried soil, three quantitative variables were investigated at two levels. These were the amount of oxidised activated charcoal (A) added to the extracting solution to remove organic interferences, the strength of CaSO4 extracting solution (C), and the time the soil was shaken with the solution (T). The aim of the investigation was to optimise the extraction procedure. The levels of the variables are given here:

		-	+
Activated charcoal (g)	A	0.5	1
CaSO4 (%)	C	0.1	0.2
Time (minutes)	T	30	60

The concentrations of nitrate-nitrogen were determined by ultra-violet spectrophotometry and compared with concentrations determined by a standard technique. The results are given below and are the amounts recovered (expressed as the percentage of known nitrate concentration).

A	C	T	Amounts	(2 Replicates)
-1	-1	-1	45.1	44.6
1	-1	-1	44.9	45.3
-1	1	-1	44.8	46.7
1	1	-1	44.7	44.8
-1	-1	1	33	35
1	-1	1	53.8	51.7
-1	1	1	32.6	33.7
1	1	1	54.2	53.2

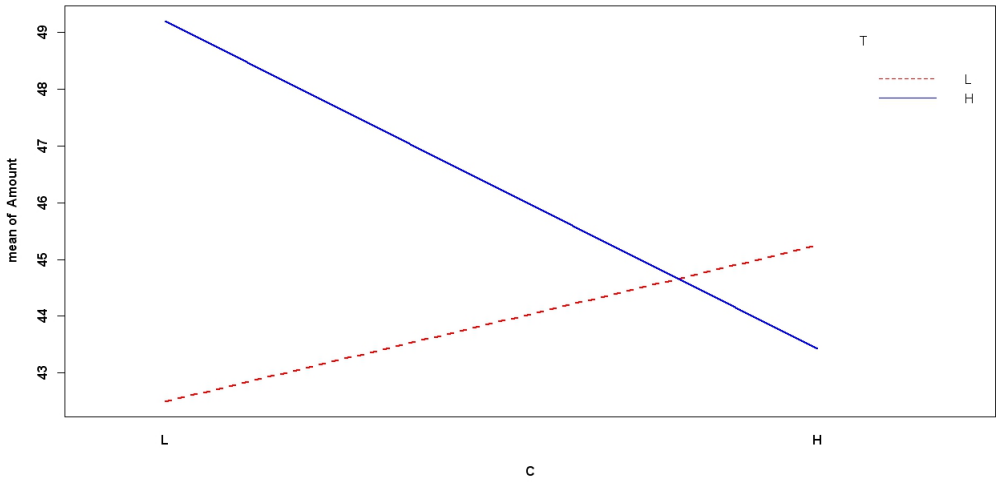
i. (8 Marks) Calculate the contrasts, the effects and the sum of squares for the effects.

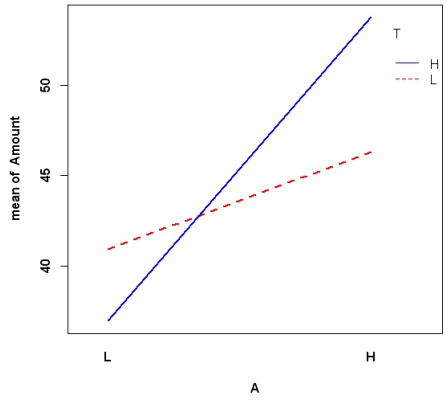
ii. (8 Marks) Using the computed sums of squares values, complete the ANOVA table (see the `R` code below).

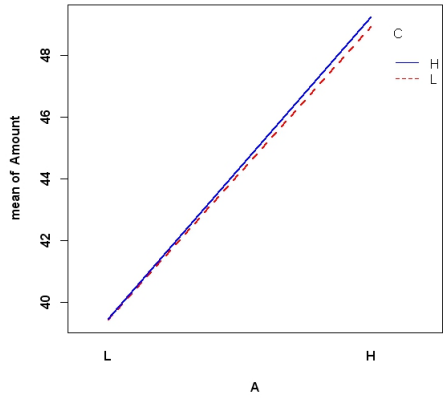
iii. (4 Marks) Comment on the tests for significant for the main effects and interactions. State clearly your conclusions.

iv. (4 Marks) Write down a regression equation that can be used predicting amounts based on the results of this experiment.

```
            Df Sum Sq Mean Sq F value     Pr(>F)
A            1    ...     ...     ...   0.000979 ***
C            1    ...     ...     ...   0.934131
T            1    ...     ...     ...   0.395554
A:C          1    ...     ...     ...   0.944243
A:T          1    ...     ...     ...   0.017582 *
C:T          1    ...     ...     ...   0.072101
A:C:T        1    ...     ...     ...   0.028522 *
Residuals    8  116.2    14.5
```







(a) Explain the following terms in the context of experimental design

i. (2 marks) levels of a factor.

ii. (2 marks) randomized block design.

(b) Six analysts each made seven determinations of the paracetamol content of the same batch of tablets. The results are shown below. There are 42 determinations in total. The mean determination for each analysts is also tabulated.

Analyst	Content						
A	84.32	84.61	84.64	84.62	84.51	84.63	84.51
B	84.24	84.13	84.00	84.02	84.25	84.41	84.30
C	84.29	84.28	84.40	84.63	84.40	84.68	84.36
D	84.14	84.48	84.27	84.22	84.22	84.02	84.33
E	84.50	83.91	84.11	83.99	83.88	84.49	84.06
F	84.70	84.36	84.61	84.15	84.17	84.11	83.81

The following `R` output has been produced as a result of analysis of these data:

`Response: Y`	`Df`	`Sum Sq`	`Mean Sq`	`F value`	$Pr(>F)$
`Analyst`	`?`	`?`	`?`	`?`	`0.00394 **`
`Residuals`	`?`	`?`	`0.04065`		
`Total`	`?`	`2.3246`			

i. (5 marks) Complete the ANOVA table in your answer sheet, replacing the "?" entries with the correct values.

ii. (2 marks) What hypothesis is being considered by this procedure.

iii. (2 marks) What is the conclusion following from the above analysis? State the null and alternative hypothesis clearly.

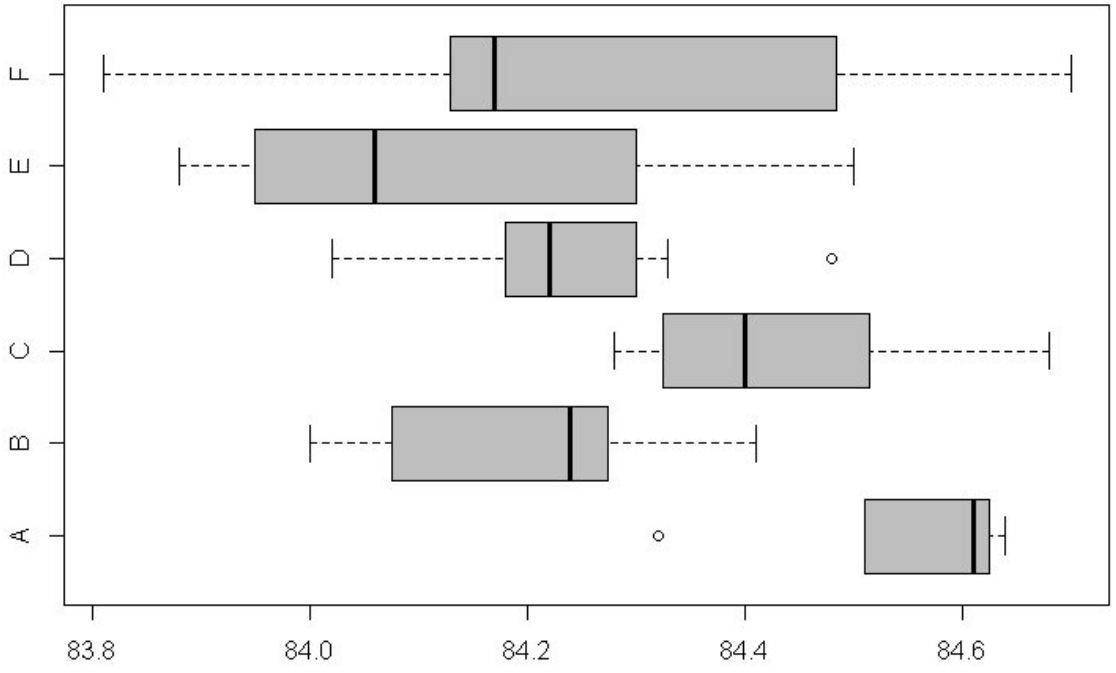
(c) The R code and graphical procedures, below and on the following page, are relevant to checking whether the underlying assumptions are met for the ANOVA model in part (b).

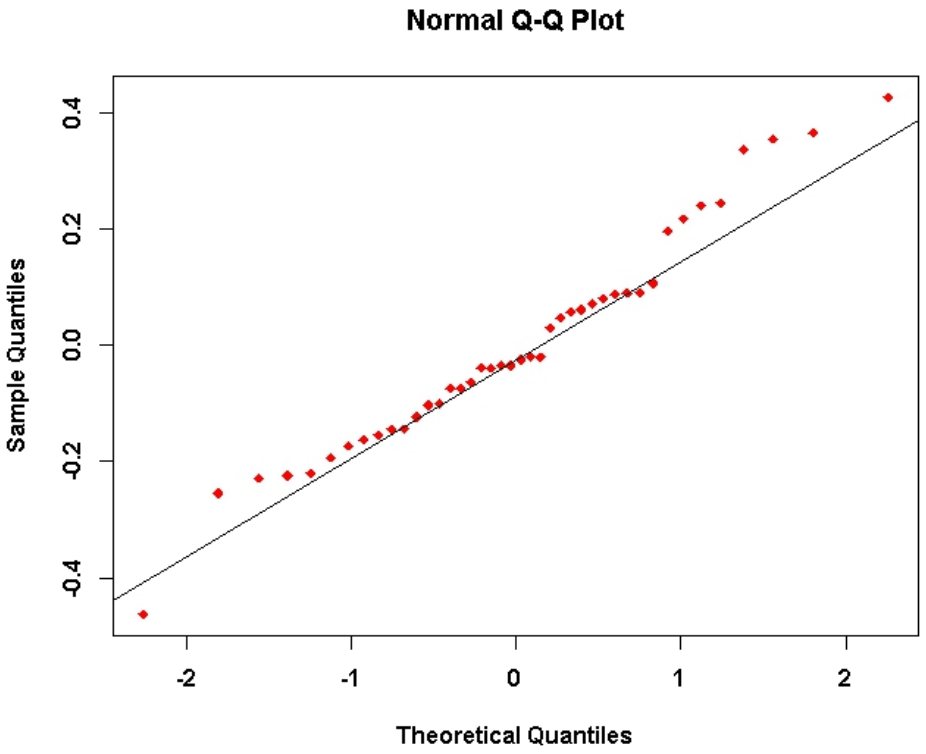
i. (3 marks) What are the assumptions underlying ANOVA?

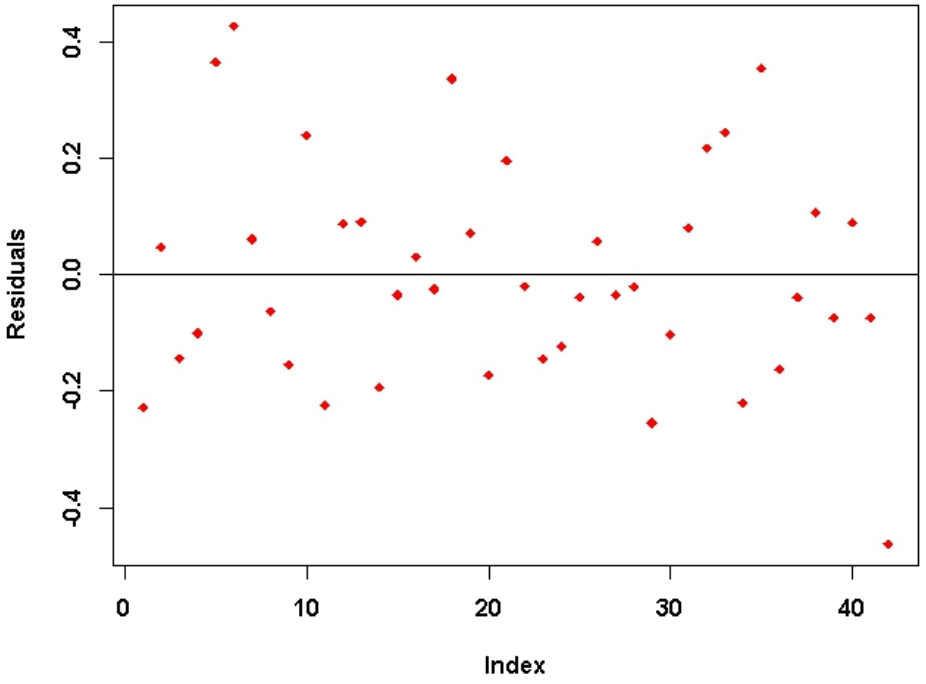
ii. (4 marks) Assess the validity of these assumptions for the ANOVA model in part(b).

```
Shapiro-Wilk normality test

data:  Residuals
W = 0.9719, p-value = 0.3819
```

```
Bartlett test of homogeneity of variances

data:  Experiment
Bartlett's K-squared = 105.9585, df = 1, p-value < 2.2e-16
```




Normal Q-Q Plot
Sample Quantiles
Theoretical Quantiles
-0.4
-0.2
0.0
0.2
0.4
-2
-1
0
1
2


Residuals
Index
-0.4
-0.2
0.0
0.2
0.4
0
10
20
30
40

Question 4. (25 marks) Testing Normality and Statistical Process Control

(a) Answer the following questions.

i. (1 marks) What is the purpose of maintaining control charts?

ii. (1 marks) What is the *Three Sigma* rule in the context of statistical process control?

iii. (4 marks) Other than applying the *Three Sigma* rule for detecting the presence of an assignable cause, what else do we look for when studying a control chart? Limit your answer to three examples. Support your answer with sketches.

iv. (2 Marks) What is a CUSUM chart? What type of departures from the production target value is this type of chart useful for detecting?

(b) A normally distributed quality characteristic is monitored through the use of control charts. These charts have the following parameters. All charts are in control.

	LCL	Centre Line	UCL
$\bar{X}$-Chart	614	620	626
R-Chart	0	8.236	18.795

i. (2 marks) What sample size is being used for this analysis?

ii. (2 marks) Estimate the standard deviation of this process.

iii. (2 marks) Compute the control limits for the process standard deviation chart (i.e. the s-chart).

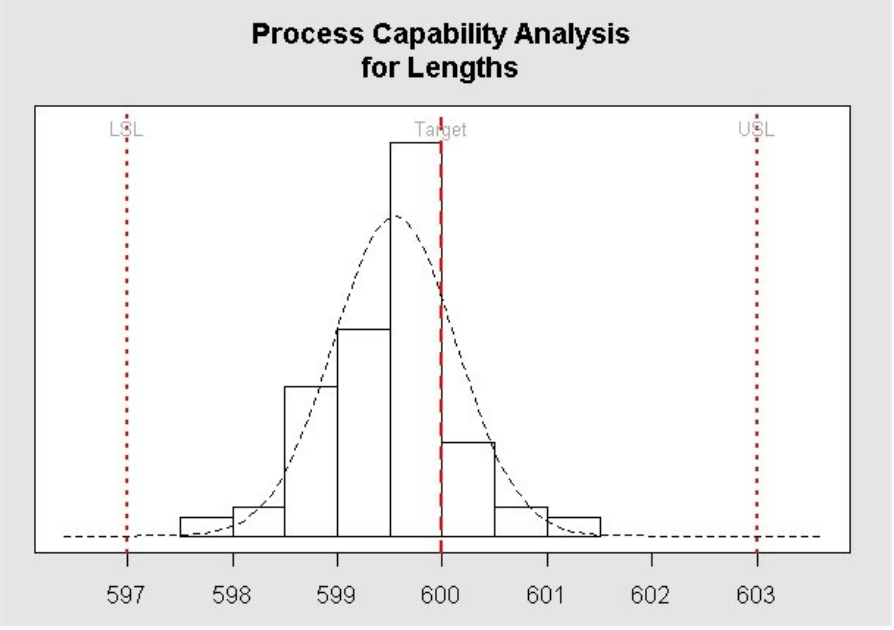
(c) An automobile assembly plant concerned about quality improvement measured sets of five camshafts on twenty occasions throughout the day. The specifications for the process state that the design specification limits at 600±3mm.

i. (2 marks) Determine the *Process Capability Indices* C_p and C_{pk}, commenting on the respective values. You may use the `R` code output on the following page.

ii. (2 marks) The value of C_{pm} is 1.353. Explain why there would be a discrepancy between C_p and C_{pm}.

iii. (2 marks) Comment on the graphical output of the *Process Capability Analysis*, also presented on the next page.

```
Process Capability Analysis

Call:
process.capability(object = obj, spec.limits = c(597, 603))
Number of obs = 100          Target = 600
Center = 599.548         LSL = 597
StdDev = 0.5846948       USL = 603

Capability indices:
Value   2.5%  97.5%
Cp     ...
Cp_l   ...
Cp_u   ...
Cp_k   ...
Cpm    1.353  1.134  1.572
Exp<LSL 0%   Obs<LSL 0%
```



Control Limits for Control Charts

$$\bar{\bar{x}} \pm 3\frac{\bar{s}}{c_4\sqrt{n}}$$

$$\bar{s} \pm 3\frac{c_5\bar{s}}{c_4}$$

$$\left[\bar{R}D_3, \bar{R}D_4\right]$$

Process Capability Indices

$$\hat{C}_p = \frac{\text{USL} - \text{LSL}}{6s}$$

$$\hat{C}_{pk} = \min\left[\frac{\text{USL} - \bar{x}}{3s}, \frac{\bar{x} - \text{LSL}}{3s}\right]$$

$$\hat{C}_{pm} = \frac{\text{USL} - \text{LSL}}{6\sqrt{s^2 + (\bar{x} - T)^2}}$$

2^3 Design: Interaction Effects

$$AB = \frac{1}{4n}\left[abc - bc + ab - b - ac + c - a + (1)\right]$$

$$AC = \frac{1}{4n}\left[(1) - a + b - ab - c + ac - bc + abc\right]$$

$$BC = \frac{1}{4n}\left[(1) + a - b - ab - c - ac + bc + abc\right]$$

$$ABC = \frac{1}{4n}\left[abc - bc - ac + c - ab + b + a - (1)\right]$$

Factorial Design: Sums of Squares

$$\text{Effect} = \frac{(\text{Contrast})}{n2^{k-1}}$$

$$\text{Sums of Squares} = \frac{(\text{Contrast})^2}{n2^k}$$

Factors for Control Charts

Sample Size (n)	c4	c5	d2	d3	D3	D4
2	0.7979	0.6028	1.128	0.853	0	3.267
3	0.8862	0.4633	1.693	0.888	0	2.574
4	0.9213	0.3889	2.059	0.88	0	2.282
5	0.9400	0.3412	2.326	0.864	0	2.114
6	0.9515	0.3076	2.534	0.848	0	2.004
7	0.9594	0.282	2.704	0.833	0.076	1.924
8	0.9650	0.2622	2.847	0.82	0.136	1.864
9	0.9693	0.2459	2.970	0.808	0.184	1.816
10	0.9727	0.2321	3.078	0.797	0.223	1.777
11	0.9754	0.2204	3.173	0.787	0.256	1.744
12	0.9776	0.2105	3.258	0.778	0.283	1.717
13	0.9794	0.2019	3.336	0.770	0.307	1.693
14	0.9810	0.1940	3.407	0.763	0.328	1.672
15	0.9823	0.1873	3.472	0.756	0.347	1.653
16	0.9835	0.1809	3.532	0.750	0.363	1.637
17	0.9845	0.1754	3.588	0.744	0.378	1.622
18	0.9854	0.1703	3.64	0.739	0.391	1.608
19	0.9862	0.1656	3.689	0.734	0.403	1.597
20	0.9869	0.1613	3.735	0.729	0.415	1.585
21	0.9876	0.1570	3.778	0.724	0.425	1.575
22	0.9882	0.1532	3.819	0.720	0.434	1.566
23	0.9887	0.1499	3.858	0.716	0.443	1.557
24	0.9892	0.1466	3.895	0.712	0.451	1.548
25	0.9896	0.1438	3.931	0.708	0.459	1.541