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DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C610 – ERM643

RESEARCH METHODS

MAY 2012 FINAL EXAMINATION

Time Allowed:

Three (3) Hours

Instructions

1. This examination has five (5) questions and one data sheet. The total number of pages is five (5) including this page.
2. Answer any four questions; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.
3. Each question is worth 25 marks.

Special Requirements

1. Data sheet.
2. Graph Paper.
3. Statistical Tables.
4. Computer, two multiplug extension cable (4 ports) and USB (4)

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

Question 1 [25]

- a) Certified reference materials are useful in the evaluation of reliability and validity of analytical data, especially when the analyte is in a complex matrix. In the determination of copper in sugar cane leaves,
- (i) What kind of certified reference materials would be suitable for this analysis? [1]
 - (ii) How would bulk sampling be carried out to source this material? [3]
 - (iii) Outline the processes that such a material would undergo during certification. [4]
 - (iv) Explain how this material would be used to evaluate validity and reliability of copper measurements in sugar cane leaves. [3]
- b) Blind samples are useful in analytical quality control in a commercial water laboratory.
- (i) What is meant by a blind sample?[1]
 - (ii) Explain how blind samples are used to evaluate validity and reliability of COD measurements in water. [3]
- c) Quality control charts are useful in ensuring that repetitive day to day measurements are under statistical control. An in-house reference material was used to generate the following data over a period of 10 days of measurement of nickel in an ore:

Day #	1	2	3	4	5	6	7	8	9	10
Ni, ppm	103	101	104	99	150	101	110	89	102	100

- (i) What is meant by an “in-house reference material”?[1]
 - (ii) Draw the quality control chart for the nickel determination, assuming that the in-house reference material is 101 ± 4 ppm Ni.[3]
 - (iii) Which days were the measurements not under statistical control and why?[2]
- d) Interlaboratory comparisons are useful in the evaluation of reliability and validity of analytical data. In the measurement of nitrates in a mine pit water sample by ion chromatography, “LAB A” ran ten replicate measurements on the sample, and requested “LAB B” to do the same with the remainder of the sample. The following results were obtained:

LAB A (ppm)	25	23	21	24	25	22	20	22	21	20
LAB B (ppm)	23	29	22	18	15	21	25	29	32	21

- (i) Comment on the validity of the results at the 95% confidence level [2]
- (ii) Comment on the relative precisions of the two laboratories at the 95% confidence level [2]

QUESTION 2 [25]

- (a) (i) Write down the equation that describes the “normal curve of error” in chemometrics, and explain all terms appearing in it.(4)
- (ii) Draw the Gaussian curve, and on it indicate the mean and standard deviation (2)
 - (iii) Under what condition in analytical sampling will the sample variance be the same as the population variance (1)

(b) (i) Differentiate between systematic error and random error in data analysis, and use an example to illustrate this difference (2)

(ii) Differentiate between precision and accuracy in research methods, and use an example to illustrate this difference (2)

(c) The following data was obtained during a spectrophotometric determination of Fe in tap water samples following complexation with bipyridine:

Triplicate absorbance readings for the standards: 1.16 ppm – 0.120, 0.125, 0.130 ; 2.32 ppm – 0.248, 0.255, 0.252;
3.48 ppm – 0.382, 0.385, 0.384 ; 4.65 ppm – 0.504, 0.506, 0.502

Triplicate absorbance readings for the sample are: 0.337, 0.335, 0.340

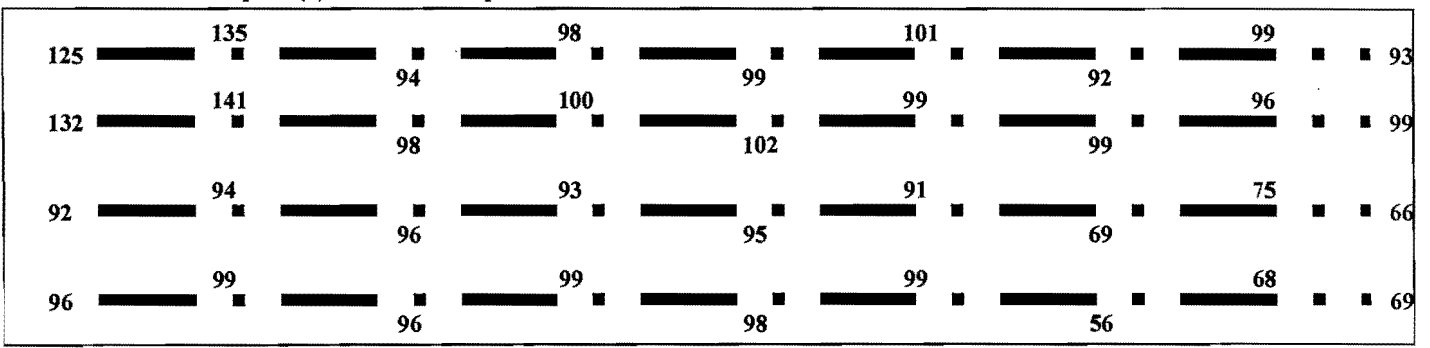
- (i) Calculate the equation of the calibration curve using the Least Squares Method (5)
- (ii) Calculate the absolute error associated with the calibration curve, S_{vc} (3)
- (iii) Calculate the absolute error associated with the analytical measurement, S_a (3)
- (iv) Calculate the absolute subsampling uncertainty, S_{ss} , in ppm units if five 500-mg portions of the sample were found to contain 3.08ppm, 3.07ppm, 3.11 ppm, 5.01 ppm, and 3.09 ppm. (2)
- (v) Is the value 5.01 ppm considered part of the data set? Explain why or why not with 90% confidence. (1)

Question 3 [25]

a) Use equations to explain the Benedetti-Pichler approach to sampling of solid samples. What are the short comings of this approach? (4)

b) River sediments present a challenge in their sampling for elemental analysis. What are these challenges, and how are they practically met? (4)

c) Thirty six (36) samples of soil were taken from a field to map the spatial variability of zinc. 500-mg portions of each sample were digested and zinc measured by AA following a standard additions procedure on the same day and same instrument as in part (a) above. The spatial distribution of zinc was found to be as follows:



- (i) Use the Kolmogorov-Smirnov test to show that the distribution of zinc in the field is not Gaussian. [6]
- (ii) What is meant by a "hot spot" or "coldspot" in analytical sampling? [2]

- (iii) In this population, identify and map the points that have resulted in a “hot spot” or “coldspot” causing the non-Gaussian distribution of zinc in the population. [2]
- (iv) Calculate the uncertainty due to the sampling operation in ppm units assuming that all other errors are relatively negligible. [2]
- (v) Use the Student’s t-test equation to determine the minimum number of samples to be taken from the population if the average value of zinc is to be within the error due to sampling at the 95% confidence level. [4]
- (vi) If the same samples gave copper results that were twice the zinc uncertainty, how would this have affected the minimum number of samples? (1)

Question 5 [25]

- a) Define the term “Principal Component Analysis, PCA”. In your brief description include uses, applications, weaknesses and any relevant detail of the technique as applied in chemometrics. [5]
- b) Data is sometimes scaled in PCA before application of the techniques. Give reasons. [2]
- c) Using the data below calculate: [4]
 - i) Eigen values
 - ii) Eigen vectors
 - iii) Loadings factors
 - iv) Score factors

Sample sites	R1	R2	R3	R4	R5
Variables					
Al	12.4	10.39	12.18	12.8	12.6
Fe	10.3	9.01	10.63	9.9	9.5

Show your working. You may use STASTICA to confirm your calculations above.

- d) Using the loadings and scores factors show: [6]
 - i) Scores plot
 - ii) Loadings plot
 - iii) Explained (%) variance plot
- e) What is the optimum number of principal components, PC’s and what is the percentage explained variance as defined by the optimum number of Principal Components? [3]
- f) Briefly discuss your findings in your principal component analysis above. In your discussion include comments on sample groups, variable groups, correlations and any observations of vital importance in your findings.[5]

Save all your working from the computer in the USB provided.

Question 6 [25 Marks]

- a) Define the term "Cluster Analysis, CA". In your brief description include uses, applications, strengths/weaknesses and any relevant details of the technique as applied in chemometrics. [10]
- b) Using the data below calculate distance matrix $d(i,k)$. [4]

$$d(i,k) = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + \dots + (x_n - x_{n+1})^2 + (y_n - y_{n+1})^2}$$

Sample sites	R1	R2	R3	R4	R5
Variables					
Ca	13.9	14.1	13.6	14.22	13.00
Na	0.3	0.2	0.2	0.13	0.18

- c) Using the average linkage method by Lance and Williams determine the clusters of the data above (in b) and draw the appropriate dendrogram. [5]

Lance and Williams equation states that:

$$d(i'2, k) = \alpha_1 d_{i1, k} + \alpha_2 d_{i2, k} + \beta d_{i1, i2} + \gamma |d_{i1, k} - d_{i2, k}|$$

where:

- α_1 is the weight between the distance of first joint object to any other object or cluster
- α_2 is the weight between the distance of second joint object to any other object or cluster
- β is the weight of the distance of both neighbouring objects
- γ is the weight of the difference between the distance of neighbouring objects or clusters.

- d) Briefly discuss your findings in your cluster analysis above. In your discussion include comments on clusters, correlations and any observations of vital importance in your findings. [6]

Show all your working. You may use excel/STASTICA to confirm your calculations above.

Save all your working from the computer in the USB provided.

Statistical tables

The following tables are presented for the convenience of the reader, and for use with the simple statistical tests, examples and exercises in this book. They are presented in a format that is compatible with the needs of analytical chemists: the significance level $P = 0.05$ has been used in most cases, and it has been assumed that the number of measurements available is fairly small. Most of these abbreviated tables have been taken, with permission, from *Elementary Statistics Tables* by Henry R. Neave, published by Routledge (Tables A.2–A.4, A.7, A.8, A.11–A.14). The reader requiring statistical data corresponding to significance levels and/or numbers of measurements not covered in the tables is referred to these sources.

Table A.1 $F(z)$, the standard normal cumulative distribution function

z	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
-3.4	0.0003	0.0003	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0005	0.0005
-3.3	0.0005	0.0005	0.0005	0.0005	0.0006	0.0006	0.0006	0.0006	0.0006	0.0007
-3.2	0.0007	0.0007	0.0007	0.0008	0.0008	0.0008	0.0008	0.0009	0.0009	0.0009
-3.1	0.0010	0.0010	0.0010	0.0011	0.0011	0.0011	0.0012	0.0012	0.0013	0.0013
-3.0	0.0013	0.0014	0.0014	0.0015	0.0015	0.0016	0.0016	0.0017	0.0018	0.0018
-2.9	0.0019	0.0019	0.0020	0.0021	0.0021	0.0022	0.0023	0.0023	0.0024	0.0025
-2.8	0.0026	0.0026	0.0027	0.0028	0.0029	0.0030	0.0031	0.0032	0.0033	0.0034
-2.7	0.0035	0.0036	0.0037	0.0038	0.0039	0.0040	0.0041	0.0043	0.0044	0.0045
-2.6	0.0047	0.0048	0.0049	0.0051	0.0052	0.0054	0.0055	0.0057	0.0059	0.0060
-2.5	0.0062	0.0064	0.0066	0.0068	0.0069	0.0071	0.0073	0.0075	0.0078	0.0080
-2.4	0.0082	0.0084	0.0087	0.0089	0.0091	0.0094	0.0096	0.0099	0.0102	0.0104
-2.3	0.0107	0.0110	0.0113	0.0116	0.0119	0.0122	0.0125	0.0129	0.0132	0.0136
-2.2	0.0139	0.0143	0.0146	0.0150	0.0154	0.0158	0.0162	0.0166	0.0170	0.0174
-2.1	0.0179	0.0183	0.0188	0.0192	0.0197	0.0202	0.0207	0.0212	0.0217	0.0222
-2.0	0.0228	0.0233	0.0239	0.0244	0.0250	0.0256	0.0262	0.0268	0.0274	0.0281

Table A.1 Continued

z	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
-1.9	0.0287	0.0294	0.0301	0.0307	0.0314	0.0322	0.0329	0.0336	0.0344	0.0351
-1.8	0.0359	0.0367	0.0375	0.0384	0.0392	0.0401	0.0409	0.0418	0.0427	0.0436
-1.7	0.0446	0.0455	0.0465	0.0475	0.0485	0.0495	0.0505	0.0516	0.0526	0.0537
-1.6	0.0548	0.0559	0.0571	0.0582	0.0594	0.0606	0.0618	0.0630	0.0643	0.0655
-1.5	0.0668	0.0681	0.0694	0.0708	0.0721	0.0735	0.0749	0.0764	0.0778	0.0793
-1.4	0.0808	0.0823	0.0838	0.0853	0.0869	0.0885	0.0901	0.0918	0.0934	0.0951
-1.3	0.0968	0.0985	0.1003	0.1020	0.1038	0.1056	0.1075	0.1093	0.1112	0.1131
-1.2	0.1151	0.1170	0.1190	0.1210	0.1230	0.1251	0.1271	0.1292	0.1314	0.1335
-1.1	0.1357	0.1379	0.1401	0.1423	0.1446	0.1469	0.1492	0.1515	0.1539	0.1562
-1.0	0.1587	0.1611	0.1635	0.1660	0.1685	0.1711	0.1736	0.1762	0.1788	0.1814
-0.9	0.1841	0.1867	0.1894	0.1922	0.1949	0.1977	0.2005	0.2033	0.2061	0.2090
-0.8	0.2119	0.2148	0.2177	0.2206	0.2236	0.2266	0.2296	0.2327	0.2358	0.2389
-0.7	0.2420	0.2451	0.2483	0.2514	0.2546	0.2578	0.2611	0.2643	0.2676	0.2709
-0.6	0.2743	0.2776	0.2810	0.2843	0.2877	0.2912	0.2946	0.2981	0.3015	0.3050
-0.5	0.3085	0.3121	0.3156	0.3192	0.3228	0.3264	0.3300	0.3336	0.3372	0.3409
-0.4	0.3446	0.3483	0.3520	0.3557	0.3594	0.3632	0.3669	0.3707	0.3745	0.3783
-0.3	0.3821	0.3859	0.3897	0.3936	0.3974	0.4013	0.4052	0.4090	0.4129	0.4168
-0.2	0.4207	0.4247	0.4286	0.4325	0.4364	0.4404	0.4443	0.4483	0.4522	0.4562
-0.1	0.4602	0.4641	0.4681	0.4721	0.4761	0.4801	0.4840	0.4880	0.4920	0.4960
0.0	0.5000	0.5040	0.5080	0.5120	0.5160	0.5199	0.5239	0.5279	0.5319	0.5359
0.1	0.5398	0.5438	0.5478	0.5517	0.5557	0.5596	0.5636	0.5675	0.5714	0.5753
0.2	0.5793	0.5832	0.5871	0.5910	0.5948	0.5987	0.6026	0.6064	0.6103	0.6141
0.3	0.6179	0.6217	0.6255	0.6293	0.6331	0.6368	0.6406	0.6443	0.6480	0.6517
0.4	0.6554	0.6591	0.6628	0.6664	0.6700	0.6736	0.6772	0.6808	0.6844	0.6879
0.5	0.6915	0.6950	0.6985	0.7019	0.7054	0.7088	0.7123	0.7157	0.7190	0.7224
0.6	0.7257	0.7291	0.7324	0.7357	0.7389	0.7422	0.7454	0.7486	0.7517	0.7549
0.7	0.7580	0.7611	0.7642	0.7673	0.7704	0.7734	0.7764	0.7794	0.7823	0.7852
0.8	0.7881	0.7910	0.7939	0.7967	0.7995	0.8023	0.8051	0.8078	0.8106	0.8133
0.9	0.8159	0.8186	0.8212	0.8238	0.8264	0.8289	0.8315	0.8340	0.8365	0.8389
1.0	0.8413	0.8438	0.8461	0.8485	0.8508	0.8531	0.8554	0.8577	0.8599	0.8621
1.1	0.8643	0.8665	0.8686	0.8708	0.8729	0.8749	0.8770	0.8790	0.8810	0.8830
1.2	0.8849	0.8869	0.8888	0.8907	0.8925	0.8944	0.8962	0.8980	0.8997	0.9015
1.3	0.9032	0.9049	0.9066	0.9082	0.9099	0.9115	0.9131	0.9147	0.9162	0.9177
1.4	0.9192	0.9207	0.9222	0.9236	0.9251	0.9265	0.9279	0.9292	0.9306	0.9319
1.5	0.9332	0.9345	0.9357	0.9370	0.9382	0.9394	0.9406	0.9418	0.9429	0.9441
1.6	0.9452	0.9463	0.9474	0.9484	0.9495	0.9505	0.9515	0.9525	0.9535	0.9545
1.7	0.9554	0.9564	0.9573	0.9582	0.9591	0.9599	0.9608	0.9616	0.9625	0.9633
1.8	0.9641	0.9649	0.9656	0.9664	0.9671	0.9678	0.9686	0.9693	0.9699	0.9706
1.9	0.9713	0.9719	0.9726	0.9732	0.9738	0.9744	0.9750	0.9756	0.9761	0.9767
2.0	0.9772	0.9778	0.9783	0.9788	0.9793	0.9798	0.9803	0.9808	0.9812	0.9817

Table A.1 Continued

<i>z</i>	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
2.1	0.9821	0.9826	0.9830	0.9834	0.9838	0.9842	0.9846	0.9850	0.9854	0.9857
2.2	0.9861	0.9864	0.9868	0.9871	0.9875	0.9878	0.9881	0.9884	0.9887	0.9890
2.3	0.9893	0.9896	0.9898	0.9901	0.9904	0.9906	0.9909	0.9911	0.9913	0.9916
2.4	0.9918	0.9920	0.9922	0.9925	0.9927	0.9929	0.9931	0.9932	0.9934	0.9936
2.5	0.9938	0.9940	0.9941	0.9943	0.9945	0.9946	0.9948	0.9949	0.9951	0.9952
2.6	0.9953	0.9955	0.9956	0.9957	0.9959	0.9960	0.9961	0.9962	0.9963	0.9964
2.7	0.9965	0.9966	0.9967	0.9968	0.9969	0.9970	0.9971	0.9972	0.9973	0.9974
2.8	0.9974	0.9975	0.9976	0.9977	0.9977	0.9978	0.9979	0.9979	0.9980	0.9981
2.9	0.9981	0.9982	0.9982	0.9983	0.9984	0.9984	0.9985	0.9985	0.9986	0.9986
3.0	0.9987	0.9987	0.9987	0.9988	0.9988	0.9989	0.9989	0.9989	0.9990	0.9990
3.1	0.9990	0.9991	0.9991	0.9991	0.9992	0.9992	0.9992	0.9992	0.9993	0.9993
3.2	0.9993	0.9993	0.9994	0.9994	0.9994	0.9994	0.9994	0.9995	0.9995	0.9995
3.3	0.9995	0.9995	0.9995	0.9996	0.9996	0.9996	0.9996	0.9996	0.9996	0.9997
3.4	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9998

Table A.2 The *t*-distribution

<i>Value of t for a confidence interval of</i>	90%	95%	98%	99%
<i>Critical value of t for P values of number of degrees of freedom</i>	0.10	0.05	0.02	0.01
1	6.31	12.71	31.82	63.66
2	2.92	4.30	6.96	9.92
3	2.35	3.18	4.54	5.84
4	2.13	2.78	3.75	4.60
5	2.02	2.57	3.36	4.03
6	1.94	2.45	3.14	3.71
7	1.89	2.36	3.00	3.50
8	1.86	2.31	2.90	3.36
9	1.83	2.26	2.82	3.25
10	1.81	2.23	2.76	3.17
12	1.78	2.18	2.68	3.05
14	1.76	2.14	2.62	2.98
16	1.75	2.12	2.58	2.92
18	1.73	2.10	2.55	2.88
20	1.72	2.09	2.53	2.85
30	1.70	2.04	2.46	2.75
50	1.68	2.01	2.40	2.68
∞	1.64	1.96	2.33	2.58

The critical values of *|t|* are appropriate for a two-tailed test. For a one-tailed test the value is taken from the column for twice the desired *P*-value, e.g. for a one-tailed test, *P* = 0.05, 5 degrees of freedom, the critical value is read from the *P* = 0.10 column and is equal to 2.02.

Table A.3 Critical values of *F* for a one-tailed test (*P* = 0.05)

<i>v</i> ₂	<i>v</i> ₁														
	1	2	3	4	5	6	7	8	9	10	12	15			
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	243.9	245.5			
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.41	19.43			
3	10.13	9.552	9.277	9.117	9.013	8.941	8.887	8.845	8.812	8.786	8.745	8.703			
4	7.709	6.944	6.591	6.388	6.256	6.163	6.094	6.041	5.999	5.964	5.912	5.858			
5	6.608	5.786	5.409	5.192	5.050	4.950	4.876	4.818	4.772	4.735	4.678	4.619			
6	5.987	5.143	4.757	4.534	4.387	4.284	4.207	4.147	4.099	4.060	4.000	3.938			
7	5.591	4.737	4.347	4.120	3.972	3.866	3.787	3.726	3.677	3.637	3.575	3.511			
8	5.318	4.459	4.066	3.838	3.687	3.581	3.500	3.438	3.388	3.347	3.284	3.218			
9	5.117	4.256	3.863	3.633	3.482	3.374	3.293	3.230	3.179	3.137	3.073	3.006			
10	4.965	4.103	3.708	3.478	3.326	3.217	3.135	3.072	3.020	2.978	2.913	2.845			
11	4.844	3.982	3.587	3.357	3.204	3.095	3.012	2.948	2.896	2.854	2.788	2.719			
12	4.747	3.885	3.490	3.259	3.106	2.996	2.913	2.849	2.796	2.753	2.687	2.617			
13	4.667	3.806	3.411	3.179	3.025	2.915	2.832	2.767	2.714	2.671	2.604	2.533			
14	4.600	3.739	3.344	3.112	2.958	2.848	2.764	2.699	2.646	2.602	2.534	2.463			
15	4.543	3.682	3.287	3.056	2.901	2.790	2.707	2.641	2.588	2.544	2.475	2.403			
16	4.494	3.634	3.239	3.007	2.852	2.741	2.657	2.591	2.538	2.494	2.425	2.352			
17	4.451	3.592	3.197	2.965	2.810	2.699	2.614	2.548	2.494	2.450	2.381	2.308			
18	4.414	3.555	3.160	2.928	2.773	2.661	2.577	2.510	2.456	2.412	2.342	2.269			
19	4.381	3.522	3.127	2.895	2.740	2.628	2.544	2.477	2.423	2.378	2.308	2.234			
20	4.351	3.493	3.098	2.866	2.711	2.599	2.514	2.447	2.393	2.348	2.278	2.203			

*v*₁ = number of degrees of freedom of the numerator and *v*₂ = number of degrees of freedom of denominator.

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ble A.4 Critical values of F for a two-tailed test ($P = 0.05$)

		v_1													
		1	2	3	4	5	6	7	8	9	10	12	15	20	
647.8	799.5	864.2	899.6	921.8	937.1	948.2	956.7	963.3	968.6	976.7	984.9	993.1			
38.51	39.00	39.17	39.25	39.30	39.33	39.36	39.37	39.39	39.40	39.41	39.43	39.45			
17.44	16.04	15.44	15.10	14.88	14.73	14.62	14.54	14.47	14.42	14.34	14.25	14.17			
12.22	10.65	9.979	9.605	9.364	9.197	9.074	8.980	8.905	8.844	8.751	8.657	8.560			
10.01	8.434	7.764	7.388	7.146	6.978	6.853	6.757	6.681	6.619	6.525	6.428	6.329			
8.813	7.260	6.599	6.227	5.988	5.820	5.695	5.600	5.523	5.461	5.366	5.269	5.168			
8.073	6.542	5.890	5.523	5.285	5.119	4.995	4.899	4.823	4.761	4.666	4.568	4.467			
7.571	6.059	5.416	5.053	4.817	4.652	4.529	4.433	4.357	4.295	4.200	4.101	3.999			
7.209	5.715	5.078	4.718	4.484	4.320	4.197	4.102	4.026	3.964	3.868	3.769	3.667			
6.937	5.456	4.826	4.468	4.236	4.072	3.950	3.855	3.779	3.717	3.621	3.522	3.419			
6.724	5.256	4.630	4.275	4.044	3.881	3.759	3.664	3.588	3.526	3.430	3.330	3.226			
6.554	5.096	4.474	4.121	3.891	3.728	3.607	3.512	3.436	3.374	3.277	3.177	3.073			
6.414	4.965	4.347	3.996	3.767	3.604	3.483	3.388	3.312	3.250	3.153	3.053	2.948			
6.298	4.857	4.242	3.892	3.663	3.501	3.380	3.285	3.209	3.147	3.050	2.949	2.844			
6.200	4.765	4.153	3.804	3.576	3.415	3.293	3.199	3.123	3.060	2.963	2.862	2.756			
6.115	4.687	4.077	3.729	3.502	3.341	3.219	3.125	3.049	2.986	2.889	2.788	2.681			
6.042	4.619	4.011	3.665	3.438	3.277	3.156	3.061	2.985	2.922	2.825	2.723	2.616			
5.978	4.560	3.954	3.608	3.382	3.221	3.100	3.005	2.929	2.866	2.769	2.667	2.559			
5.922	4.508	3.903	3.559	3.333	3.172	3.051	2.956	2.880	2.817	2.720	2.617	2.509			
5.871	4.461	3.859	3.515	3.289	3.128	3.007	2.913	2.837	2.774	2.676	2.573	2.464			

number of degrees of freedom of the numerator and $v_2 =$ number of degrees of freedom of the denominator.

Table A.5 Critical values of Q ($P = 0.05$) for a two-sided test

Sample size	Critical value
4	0.831
5	0.717
6	0.621
7	0.570

Taken from King, E. P. 1958. *J. Am. Statist. Assoc.*, 48: 531.

Table A.6 Critical values of G ($P = 0.05$) for a two-sided test

Sample size	Critical value
3	1.155
4	1.481
5	1.715
6	1.887
7	2.020
8	2.126
9	2.215
10	2.290

Taken from *Outliers in Statistical Data*, Vic Barnett and Toby Lewis, 2nd Edition, 1984, John Wiley & Sons Limited.

Table A.7 Critical values of X^2 ($P = 0.05$)

Number of degrees of freedom	Critical value
1	3.84
2	5.99
3	7.81
4	9.49
5	11.07
6	12.59
7	14.07
8	15.51
9	16.92
10	18.31

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Table A.13 The Spearman rank correlation coefficient. Critical values for ρ at $P = 0.05$

n	One-tailed test	Two-tailed test
5	0.900	1.000
6	0.829	0.886
7	0.714	0.786
8	0.643	0.738
9	0.600	0.700
10	0.564	0.649
11	0.536	0.618
12	0.504	0.587
13	0.483	0.560
14	0.464	0.538
15	0.446	0.521
16	0.429	0.503
17	0.414	0.488
18	0.401	0.472
19	0.391	0.460
20	0.380	0.447

Table A.14 The Kolmogorov test. Critical two-tailed values for a specified distribution, and for unspecified normal distributions, at $P = 0.05$

n	Specified distributions	Unspecified normal distributions
3	0.708	0.376
4	0.624	0.375
5	0.563	0.343
6	0.519	0.323
7	0.483	0.304
8	0.454	0.288
9	0.430	0.274
10	0.409	0.262
11	0.391	0.251
12	0.375	0.242
13	0.361	0.234
14	0.349	0.226
15	0.338	0.219
16	0.327	0.213
17	0.318	0.207
18	0.309	0.202
19	0.301	0.197
20	0.294	0.192

The appropriate value is compared with the maximum difference between the experimental and theoretical cumulative frequency curves, as described in the text.

Table A.15 Critical values for C ($P = 0.05$) for $n = 2$

k	Critical value
3	0.967
4	0.906
5	0.841
6	0.781
7	0.727
8	0.680
9	0.638
10	0.602

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TABLE B Critical values of Student's *t*-distribution

$\nu \backslash \alpha$	0.9	0.5	0.4	0.2	0.1	0.05	0.02	0.01	0.001	$\alpha \backslash \nu$
1	.158	1.000	1.376	3.078	6.314	12.706	31.821	63.657	636.619	1
2	.142	.816	1.061	1.886	2.920	4.303	6.965	9.925	31.598	2
3	.137	.765	.978	1.638	2.353	3.182	4.541	5.841	12.924	3
4	.134	.741	.941	1.533	2.132	2.776	3.747	4.604	8.610	4
5	.132	.727	.920	1.476	2.015	2.571	3.365	4.032	6.869	5
6	.131	.718	.906	1.440	1.943	2.447	3.143	3.707	5.959	6
7	.130	.711	.896	1.415	1.895	2.365	2.998	3.499	5.408	7
8	.130	.706	.889	1.397	1.860	2.306	2.896	3.355	5.041	8
9	.129	.703	.883	1.383	1.833	2.262	2.821	3.250	4.781	9
10	.129	.700	.879	1.372	1.812	2.228	2.764	3.169	4.587	10
11	.129	.697	.876	1.363	1.796	2.201	2.718	3.106	4.437	11
12	.128	.695	.873	1.356	1.782	2.179	2.681	3.055	4.318	12
13	.128	.694	.870	1.350	1.771	2.160	2.650	3.012	4.221	13
14	.128	.692	.868	1.345	1.761	2.145	2.624	2.977	4.140	14
15	.128	.691	.866	1.341	1.753	2.131	2.602	2.947	4.073	15
16	.128	.690	.865	1.337	1.746	2.120	2.583	2.921	4.015	16
17	.128	.689	.863	1.333	1.740	2.110	2.567	2.898	3.965	17
18	.127	.688	.862	1.330	1.734	2.101	2.552	2.878	3.922	18
19	.127	.688	.861	1.328	1.729	2.093	2.539	2.861	3.883	19
20	.127	.687	.860	1.325	1.725	2.086	2.528	2.845	3.850	20
21	.127	.686	.859	1.323	1.721	2.080	2.518	2.831	3.819	21
22	.127	.686	.858	1.321	1.717	2.074	2.508	2.819	3.792	22
23	.127	.685	.858	1.319	1.714	2.069	2.500	2.807	3.767	23
24	.127	.685	.857	1.318	1.711	2.064	2.492	2.797	3.745	24
25	.127	.684	.856	1.316	1.708	2.060	2.485	2.787	3.725	25
26	.127	.684	.856	1.315	1.706	2.056	2.479	2.779	3.707	26
27	.127	.684	.855	1.314	1.703	2.052	2.473	2.771	3.690	27
28	.127	.683	.855	1.313	1.701	2.048	2.467	2.763	3.674	28
29	.127	.683	.854	1.311	1.699	2.045	2.462	2.756	3.659	29
30	.127	.683	.854	1.310	1.697	2.042	2.457	2.750	3.646	30
40	.126	.681	.851	1.303	1.684	2.021	2.423	2.704	3.551	40
60	.126	.679	.848	1.296	1.671	2.000	2.390	2.660	3.460	60
120	.126	.677	.845	1.289	1.658	1.980	2.358	2.617	3.373	120
∞	.126	.674	.842	1.282	1.645	1.960	2.326	2.576	3.291	∞

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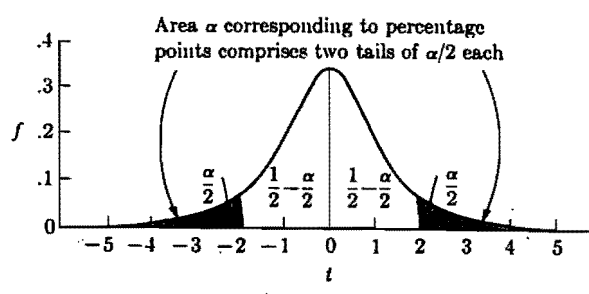


TABLE X Critical values of the δ -corrected one-sample Kolmogorov-Smirnov statistic

n	δ	α				
		0.2	0.1	0.05	0.02	0.01
3	0.0	.35477	.41811	.46702	.53456	.57900
	0.5	.39814	.46938	.54093	.61789	.66234
	1.0	.53584	.63160	.70760	.78456	.82900
4	0.0	.33435	.39075	.44641	.50495	.54210
	0.5	.36765	.44022	.49894	.56387	.60924
	1.0	.46154	.53829	.60468	.68377	.73409
5	0.0	.31556	.37359	.42174	.47692	.51576
	0.5	.34698	.40945	.46328	.52718	.56853
	1.0	.41172	.48153	.54273	.61133	.65692
6	0.0	.30244	.35522	.40045	.45440	.48988
	0.5	.32704	.38466	.43593	.49407	.53327
	1.0	.37706	.44074	.49569	.55969	.60287
7	0.0	.28991	.33905	.38294	.43337	.46761
	0.5	.31005	.36464	.41200	.46701	.50438
	1.0	.35066	.40892	.46010	.51968	.55970
8	0.0	.27828	.32538	.36697	.41522	.44819
	0.5	.29581	.34712	.39177	.44404	.47929
	1.0	.32925	.38365	.43160	.48732	.52519
9	0.0	.26794	.31325	.35277	.39922	.43071
	0.5	.28355	.33191	.37446	.42404	.45776
	1.0	.31157	.36287	.40794	.46067	.49652
10	0.0	.25884	.30221	.34022	.38481	.41517
	0.5	.27260	.31866	.35925	.40662	.43893
	1.0	.29668	.34525	.38798	.43809	.47220
11	0.0	.25071	.29227	.32894	.37187	.40122
	0.5	.26284	.30697	.34577	.39125	.42225
	1.0	.28388	.33008	.37084	.41864	.45127
12	0.0	.24325	.28330	.31869	.36019	.38856
	0.5	.25410	.29648	.33376	.37751	.40738
	1.0	.27269	.31686	.35588	.40167	.43298
13	0.0	.23639	.27515	.30935	.34954	.37703
	0.5	.24624	.28703	.32297	.36516	.39401
	1.0	.26279	.30520	.34265	.38668	.41680
14	0.0	.23010	.26767	.30081	.33980	.36649
	0.5	.23909	.27846	.31319	.35398	.38190
	1.0	.25395	.29478	.33086	.37331	.40238
15	0.0	.22430	.26077	.29296	.33083	.35679
	0.5	.23255	.27064	.30426	.34379	.37087
	1.0	.24600	.28541	.32026	.36128	.38940
16	0.0	.21895	.25439	.28570	.32256	.34784
	0.5	.22653	.26347	.29608	.33446	.36076
	1.0	.23879	.27692	.31065	.35039	.37764
17	0.0	.21397	.24847	.27897	.31489	.33953
	0.5	.22098	.25686	.28855	.32586	.35145
	1.0	.23221	.26918	.30189	.34045	.36691
18	0.0	.20933	.24296	.27270	.30775	.33181
	0.5	.21582	.25073	.28158	.31792	.34284
	1.0	.22617	.26208	.29386	.33134	.35707
19	0.0	.20498	.23781	.26685	.30108	.32459
	0.5	.21103	.24504	.27511	.31054	.33485
	1.0	.22060	.25553	.28646	.32295	.34801
20	0.0	.20089	.23298	.26137	.29484	.31784
	0.5	.20656	.23973	.26908	.30366	.32741
	1.0	.21544	.24947	.27961	.31518	.33962
21	0.0	.19705	.22844	.25622	.28898	.31149
	0.5	.20236	.23477	.26343	.29723	.32045
	1.0	.21064	.24384	.27325	.30796	.33182

TABLE X Critical values of the δ -corrected one-sample Kolmogorov-Smirnov statistic (continued)

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n	δ	0.2
22	0.0	.19343
	0.5	.19843
23	0.0	.19001
	0.5	.19472
24	0.0	.18677
	0.5	.19121
25	0.0	.18370
	0.5	.18790
26	0.0	.18077
	0.5	.18476
27	0.0	.17799
	0.5	.18178
28	0.0	.17533
	0.5	.17894
29	0.0	.17280
	0.5	.17624
30	0.0	.17037
	0.5	.17365
31	0.0	.16805
	0.5	.17119
32	0.0	.16582
	0.5	.16882
33	0.0	.16368
	0.5	.16656
34	0.0	.16162
	0.5	.16439
35	0.0	.15964
	0.5	.16230
36	0.0	.15774
	0.5	.16029
37	0.0	.15590
	0.5	.15836
38	0.0	.15413
	0.5	.15650
39	0.0	.15242
	0.5	.15471
40	0.0	.15076
	0.5	.15297
1.0	.15622	

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TABLE X Critical values of the δ -corrected one-sample Kolmogorov-Smirnov statistic (continued)

		α						
0.02	0.01	n	δ	0.2	0.1	0.05	0.02	0.01
1456	.57900	22	0.0	.19343	.22416	.25136	.28346	.30552
1789	.66234		0.5	.19843	.23011	.25814	.29121	.31393
1456	.82900		1.0	.20616	.23859	.26732	.30123	.32456
1495	.54210	23	0.0	.19001	.22012	.24679	.27825	.29989
1387	.60924		0.5	.19472	.22572	.25317	.28554	.30780
1377	.73409		1.0	.20197	.23367	.26176	.29494	.31776
1692	.51576	24	0.0	.18677	.21630	.24245	.27333	.29456
1718	.56853		0.5	.19121	.22159	.24847	.28021	.30202
133	.65692		1.0	.19804	.22906	.25656	.28904	.31138
1440	.48988	25	0.0	.18370	.21268	.23835	.26866	.28951
1407	.53327		0.5	.18790	.21768	.24404	.27516	.29657
1969	.60287		1.0	.19433	.22472	.25166	.28349	.30539
1337	.46761	26	0.0	.18077	.20924	.23445	.26423	.28472
1701	.50438		0.5	.18476	.21397	.23984	.27039	.29140
968	.55970		1.0	.19084	.22063	.24704	.27825	.29973
522	.44819	27	0.0	.17799	.20596	.23074	.26001	.28016
404	.47929		0.5	.18178	.21046	.23586	.26586	.28650
732	.52519		1.0	.18753	.21676	.24267	.27330	.29439
922	.43071	28	0.0	.17533	.20283	.22721	.25600	.27582
404	.45776		0.5	.17894	.20712	.23208	.26156	.28185
067	.49652		1.0	.18440	.21309	.23853	.26861	.28933
481	.41517	29	0.0	.17280	.19985	.22383	.25217	.27168
1662	.43893		0.5	.17624	.20393	.22847	.25747	.27742
809	.47220		1.0	.18142	.20961	.23461	.26417	.28452
187	.40122	30	0.0	.17037	.19700	.22061	.24851	.26772
125	.42225		0.5	.17365	.20090	.22504	.25356	.27320
864	.45127		1.0	.17859	.20630	.23088	.25994	.27996
1019	.38856	31	0.0	.16805	.19427	.21752	.24501	.26393
751	.40738		0.5	.17119	.19800	.22176	.24983	.26917
1167	.43298		1.0	.17589	.20314	.22732	.25591	.27561
1954	.37703	32	0.0	.16582	.19166	.21457	.24165	.26030
516	.39401		0.5	.16882	.19522	.21862	.24627	.26531
1668	.41680		1.0	.17332	.20014	.22393	.25207	.27146
1980	.36649	33	0.0	.16368	.18915	.21173	.23843	.25683
1398	.38190		0.5	.16656	.19256	.21561	.24286	.26162
1331	.40238		1.0	.17086	.19726	.22069	.24840	.26750
1083	.35679	34	0.0	.16162	.18674	.20901	.23534	.25348
1379	.37087		0.5	.16439	.19001	.21273	.23958	.25808
1128	.38940		1.0	.16850	.19451	.21759	.24490	.26371
1256	.34784	35	0.0	.15964	.18442	.20639	.23237	.25027
1446	.36076		0.5	.16230	.18756	.20996	.23644	.25469
1039	.37764		1.0	.16625	.19188	.21462	.24154	.26008
1489	.33953	36	0.0	.15774	.18218	.20387	.22951	.24718
1586	.35145		0.5	.16029	.18521	.20730	.23343	.25143
1045	.36691		1.0	.16408	.18935	.21178	.23831	.25660
1775	.33181	37	0.0	.15590	.18003	.20144	.22676	.24421
1792	.34284		0.5	.15836	.18294	.20474	.23052	.24829
1134	.35707		1.0	.16200	.18692	.20904	.23522	.25326
1108	.32459	38	0.0	.15413	.17796	.19910	.22410	.24134
1054	.33485		0.5	.15650	.18076	.20228	.22773	.24527
1295	.34801		1.0	.16000	.18459	.20642	.23225	.25005
1484	.31784	39	0.0	.15242	.17595	.19684	.22154	.23857
1366	.32741		0.5	.15471	.17866	.19991	.22504	.24236
518	.33962		1.0	.15808	.18234	.20389	.22938	.24696
1898	.31149	40	0.0	.15076	.17402	.19465	.21907	.23589
1723	.32045		0.5	.15297	.17663	.19762	.22244	.23955
1796	.33182		1.0	.15622	.18018	.20145	.22663	.24399