

DEPARTMENT OF CHEMISTRY**UNIVERSITY OF ESWATINI****CHE 604****RESEARCH METHODS IN CHEMISTRY****MAY 2019 FINAL EXAMINATION****Time Allowed:** Three (3) Hours**Instructions**

1. This examination has six (6) questions and one data sheet. The total number of pages is five (5) including this page.
2. Answer any four (4) 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.

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QUESTION 1 [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 (3)
- (iii) Under what conditions in analytical sampling will the sample variance be the same as the population variance (2)
- (b) Use equations to explain the Benedetti-Pichler approach to sampling of solid samples. What are the short comings of this approach? (4)
- (c) River sediments present a challenge in their sampling for elemental analysis. What are these challenges, and how are they practically met? (4)
- (d) Describe Gy’s approach to sampling heterogeneous samples (4)
- (e) Describe Visman’s approach to sampling coal in a moving belt. (4)

QUESTION 2 [25]

- (a) A new microwave method for the analysis of carbon dioxide is being evaluated by comparing the results obtained using it with that of the standard method. The results of the concentrations of the gas (in $\mu\text{L}/\text{m}^3$), by the two methods are as shown in the table below:

Standard Method	Microwave Method
216	215
242	223
216	215
235	213
231	257
243	246
	221
	236
	231

- (i) Is there a significant difference between the two methods at the 95% confidence level. (5)
- (ii) Comment on the precision of the microwave method relative to the standard one at 95% confidence level. (3)
- (b) (i) Explain the difference between “homogeneous” and “heterogeneous” samples. (3)
- (ii) Discuss the challenges associated with the latter with respect to the sampling step in chemical analysis. (4)
- (c) In chemical research, the encoding and decoding of analytical information affects the accuracy and precision of research data.
- (i) Use diagrams to explain how a carbon dioxide laser works in encoding analytical information. (5)
- (ii) Use diagrams to explain how the Si-VIDICON image sensor works in decoding analytical information. (5)

QUESTION 3 [25]

- (a) Use diagrams to explain how the ORTHICON image sensor works in decoding analytical information. (5)
- (b) (i) Use a diagram to explain what is meant by aliasing? (4)
- (ii) Apply the Nyquist Theorem to explain how aliasing can be avoided. (3)
- (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)

QUESTION 4 [25]

- (a) The following absorbance data was obtained in triplicate during a standard additions determination of zinc in a soil sample using atomic absorption, AA, following classical dissolution of 500-mg portions:

Addition 0: **0.102**

Addition 1: **0.149**

Addition 2: **0.205**

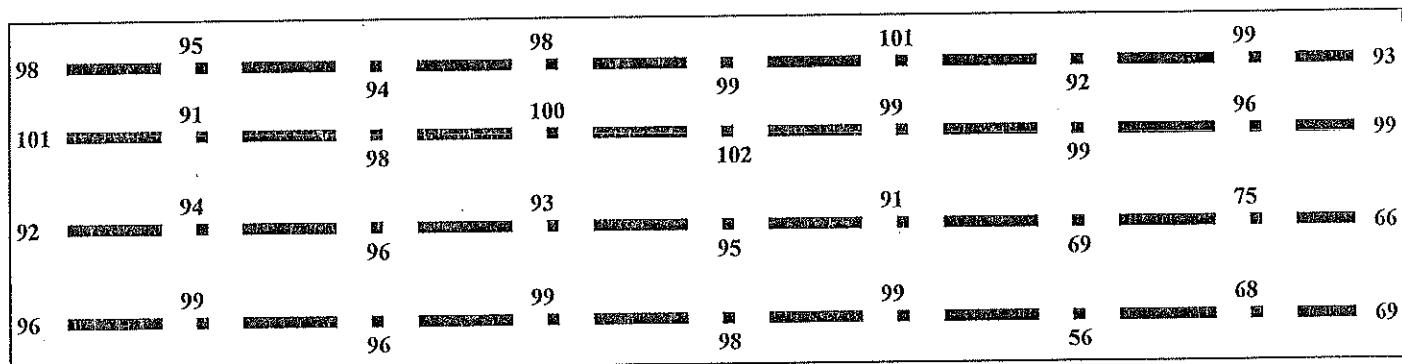
Addition 3: **0.246**

where 0 μ L, 5 μ L, 10 μ L, and 15 μ L of a 100 ppm Zn standard solution was added to 10-mL aliquots of sample, respectively.

- (i) Perform a linear regression on the calibration curve using the least squares method (4)

- (ii) Calculate the relative error, in %, associated with the intercept, S_{vc} (4)

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 the 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:



- (iii) Use the Kolmogorov-Smirnoff test to show that the distribution of zinc in the field is not Gaussian. (7)
- (iv) 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)
- (v) Calculate the uncertainty due to the sampling operation in ppm units (4)
- (vi) 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)

QUESTION 5 [25]

- (a) In data acquisition, noise is an important concept in instrumental analysis as it is a predominant factor in determining precision and detection limits.
- (i) Explain what is meant by “signal” in analytical data acquisition? (2)
 - (ii) Explain what is meant by “noise” in analytical data acquisition? (2)
 - (iii) Define “signal-to-noise ratio” in analytical data acquisition? (4)
 - (iv) Give the operational definition of “detection limit”. (3)
- (b) With regard to Johnson Noise,
- (i) Explain its origins in analytical instrumentation (3)
 - (ii) Write down the equation relating the magnitude of this noise to the bandwidth, and explain all terms appearing in it (4)
- (c) With regard to Shot Noise,
- (i) Explain its origins in analytical instrumentation (3)
 - (ii) Write down the equation relating the magnitude of this noise to the bandwidth, and explain all terms appearing in it (4)

QUESTION 6 [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. Explain how this material would be used to evaluate the validity and reliability of copper measurements in sugar cane leaves. (5)
- (b) Blind samples are useful in analytical quality control in a commercial water laboratory.
- (i) What is meant by a blind sample? (2)
 - (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”? (3)

(ii) Draw the quality control chart for the nickel determination, assuming that the in-house reference material is 101 ± 4 ppm Ni. Which days were the measurements not under statistical control and why? (6)

(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. (3)

(ii) Comment on the relative precisions of the two laboratories at the 95% confidence level. (3)

Table 26-5 VALUES OF F AT THE
95% CONFIDENCE LEVEL

v_2	v_1					
	2	3	4	5	6	∞
2	19.00	19.16	19.25	19.30	19.33	19.50
3	9.55	9.28	9.12	9.01	8.94	8.53
4	6.94	6.59	6.39	6.26	6.16	5.63
5	5.79	5.41	5.19	5.05	4.95	4.36
6	5.14	4.76	4.53	4.39	4.28	3.67
∞	3.00	2.60	2.37	2.21	2.10	1.00

Table 4-2
Values of Student's t

Degrees of freedom	Confidence level (%)				
	50	80	90	95	99
1	1.000	3.078	6.314	12.706	63.657
2	0.816	1.886	2.920	4.301	9.925
3	0.765	1.638	2.353	3.182	5.841
4	0.741	1.533	2.132	2.776	4.604
5	0.727	1.476	2.015	2.571	4.032
6	0.718	1.440	1.943	2.447	3.707
7	0.711	1.415	1.895	2.365	3.500
8	0.706	1.397	1.860	2.306	3.355
9	0.703	1.383	1.833	2.262	3.250
10	0.700	1.372	1.812	2.228	3.169
15	0.691	1.341	1.753	2.131	2.947
20	0.687	1.325	1.725	2.086	2.845
∞	0.674	1.282	1.645	1.960	2.576

Table 4-4
Values of Q for rejection of data

Q (90% confidence)	0.94	0.76	0.64	0.56	0.51	0.47	0.44	0.41
Number of observations	3	4	5	6	7	8	9	10

TABLE D Critical values of the chi-square distribution

$\nu \backslash \alpha$.995	.975	.9	.5	.1	.05	.025	.01	.005	.001	α / ν
1	0.000	0.000	0.016	0.455	2.706	3.841	5.024	6.635	7.879	10.828	1
2	0.010	0.051	0.211	1.386	4.605	5.991	7.378	9.210	10.597	13.816	2
3	0.072	0.216	0.584	2.366	6.251	7.815	9.348	11.345	12.838	16.266	3
4	0.207	0.484	1.064	3.357	7.779	9.488	11.143	13.277	14.860	18.467	4
5	0.412	0.831	1.610	4.351	9.236	11.070	12.832	15.086	16.750	20.515	5
6	0.676	1.237	2.204	5.348	10.645	12.592	14.449	16.812	18.548	22.458	6
7	0.989	1.690	2.833	6.346	12.017	14.067	16.013	18.475	20.278	24.322	7
8	1.344	2.180	3.490	7.344	13.362	15.507	17.535	20.090	21.955	26.124	8
9	1.735	2.700	4.168	8.343	14.684	16.919	19.023	21.666	23.589	27.877	9
10	2.156	3.247	4.865	9.342	15.987	18.307	20.483	23.209	25.188	29.588	10
11	2.603	3.816	5.578	10.341	17.275	19.675	21.920	24.725	26.757	31.264	11
12	3.074	4.404	6.304	11.340	18.549	21.026	23.337	26.217	28.300	32.910	12
13	3.565	5.009	7.042	12.340	19.812	22.362	24.736	27.688	29.819	34.528	13
14	4.075	5.629	7.790	13.339	21.064	23.685	26.119	29.141	31.319	36.123	14
15	4.601	6.262	8.547	14.339	22.307	24.996	27.488	30.578	32.801	37.697	15
16	5.142	6.908	9.312	15.338	23.542	26.296	28.845	32.000	34.267	39.252	16
17	5.697	7.564	10.085	16.338	24.769	27.587	30.191	33.409	35.718	40.790	17
18	6.265	8.231	10.865	17.338	25.989	28.869	31.526	34.805	37.156	42.312	18
19	6.844	8.907	11.651	18.338	27.204	30.144	32.852	36.191	38.582	43.820	19
20	7.434	9.591	12.443	19.337	28.412	31.410	34.170	37.566	39.997	45.315	20
21	8.034	10.283	13.240	20.337	29.615	32.670	35.479	38.932	41.401	46.797	21
22	8.643	10.982	14.042	21.337	30.813	33.924	36.781	40.289	42.796	48.268	22
23	9.260	11.688	14.848	22.337	32.007	35.172	38.076	41.638	44.181	49.728	23
24	9.886	12.401	15.659	23.337	33.196	36.415	39.364	42.980	45.558	51.179	24
25	10.520	13.120	16.473	24.337	34.382	37.652	40.646	44.314	46.928	52.620	25
26	11.160	13.844	17.292	25.336	35.563	38.885	41.923	45.642	48.290	54.052	26
27	11.808	14.573	18.114	26.336	36.741	40.113	43.194	46.963	49.645	55.476	27
28	12.461	15.308	18.939	27.336	37.916	41.337	44.461	48.278	50.993	56.892	28
29	13.121	16.047	19.768	28.336	39.088	42.557	45.722	49.588	52.336	58.301	29
30	13.787	16.791	20.599	29.336	40.256	43.773	46.979	50.892	53.672	59.703	30
31	14.458	17.539	21.434	30.336	41.422	44.985	48.232	52.191	55.003	61.098	31
32	15.134	18.291	22.271	31.336	42.585	46.194	49.480	53.486	56.329	62.487	32
33	15.815	19.047	23.110	32.336	43.745	47.400	50.725	54.776	57.649	63.870	33
34	16.501	19.806	23.952	33.336	44.903	48.602	51.966	56.061	58.964	65.247	34
35	17.192	20.569	24.797	34.336	46.059	49.802	53.203	57.342	60.275	66.619	35
36	17.887	21.336	25.643	35.336	47.212	50.998	54.437	58.619	61.582	67.985	36
37	18.586	22.106	26.492	36.335	48.363	52.192	55.668	59.892	62.884	69.346	37
38	19.289	22.878	27.343	37.335	49.513	53.384	56.896	61.162	64.182	70.703	38
39	19.996	23.654	28.196	38.335	50.660	54.572	58.120	62.428	65.476	72.055	39
40	20.707	24.433	29.051	39.335	51.805	55.758	59.342	63.691	66.766	73.402	40
41	21.421	25.215	29.907	40.335	52.949	56.942	60.561	64.950	68.053	74.745	41
42	22.138	25.999	30.765	41.335	54.090	58.124	61.777	66.206	69.336	76.084	42
43	22.859	26.785	31.625	42.335	55.230	59.304	62.990	67.459	70.616	77.419	43
44	23.584	27.575	32.487	43.335	56.369	60.481	64.202	68.710	71.893	78.750	44
45	24.311	28.366	33.350	44.335	57.505	61.656	65.410	69.957	73.166	80.077	45
46	25.042	29.160	34.215	45.335	58.641	62.830	66.617	71.201	74.437	81.400	46
47	25.775	29.956	35.081	46.335	59.774	64.001	67.821	72.443	75.704	82.720	47
48	26.511	30.755	35.949	47.335	60.907	65.171	69.023	73.683	76.969	84.037	48
49	27.249	31.555	36.818	48.335	62.038	66.339	70.222	74.919	78.231	85.351	49
50	27.991	32.357	37.689	49.335	63.167	67.505	71.420	76.154	79.490	86.661	50

TABLE D Critical val

$\nu \backslash \alpha$.995	.975	.9
51	28.735	33.162	38.560
52	29.481	33.968	39.433
53	30.230	34.776	40.308
54	30.981	35.586	41.183
55	31.735	36.398	42.060
56	32.490	37.212	42.931
57	33.248	38.027	43.810
58	34.008	38.844	44.690
59	34.770	39.662	45.571
60	35.534	40.482	46.451
61	36.300	41.303	47.341
62	37.068	42.126	48.221
63	37.838	42.950	49.111
64	38.610	43.776	49.990
65	39.383	44.603	50.880
66	40.158	45.431	51.771
67	40.935	46.261	52.651
68	41.713	47.092	53.541
69	42.494	47.924	54.431
70	43.275	48.758	55.321
71	44.058	49.592	56.221
72	44.843	50.428	57.111
73	45.629	51.265	58.000
74	46.417	52.103	58.900
75	47.206	52.942	59.791
76	47.997	53.782	60.611
77	48.788	54.623	61.511
78	49.582	55.466	62.411
79	50.376	56.309	63.311
80	51.172	57.153	64.211
81	51.969	57.998	65.111
82	52.767	58.845	66.011
83	53.567	59.692	66.911
84	54.368	60.540	67.811
85	55.170	61.389	68.711
86	55.973	62.239	69.611
87	56.777	63.089	70.511
88	57.582	63.941	71.411
89	58.389	64.793	72.311
90	59.196	65.647	73.211
91	60.005	66.501	74.111
92	60.815	67.356	75.111
93	61.625	68.211	76.011
94	62.437	69.068	76.911
95	63.250	69.925	77.811
96	64.063	70.783	78.711
97	64.878	71.642	79.611
98	65.694	72.501	80.411
99	66.510	73.361	81.211
100	67.328	74.222	82.111

portion

TABLE D Critical values of the chi-square distribution (*continued*)

1	.005	.001	α/ν	ν	.995	.975	.9	.5	.1	.05	.025	.01	.005	.001	α/ν
35	7.879	10.828	1	51	28.735	33.162	38.560	50.335	64.295	68.669	72.616	77.386	80.747	87.968	51
10	10.597	13.816	2	52	29.481	33.968	39.433	51.335	65.422	69.832	73.810	78.616	82.001	89.272	52
45	12.838	16.266	3	53	30.230	34.776	40.308	52.335	66.548	70.993	75.002	79.843	83.253	90.573	53
77	14.860	18.467	4	54	30.981	35.586	41.183	53.335	67.673	72.153	76.192	81.069	84.502	91.872	54
86	16.750	20.515	5	55	31.735	36.398	42.060	54.335	68.796	73.311	77.380	82.292	85.749	93.168	55
12	18.548	22.458	6	56	32.490	37.212	42.937	55.335	69.918	74.468	78.567	83.513	86.994	94.460	56
75	20.278	24.322	7	57	33.248	38.027	43.816	56.335	71.040	75.624	79.752	84.733	88.237	95.751	57
90	21.955	26.124	8	58	34.008	38.844	44.696	57.335	72.160	76.778	80.936	85.950	89.477	97.039	58
66	23.589	27.877	9	59	34.770	39.662	45.577	58.335	73.279	77.931	82.117	87.166	90.715	98.324	59
09	25.188	29.588	10	60	35.534	40.482	46.459	59.335	74.397	79.082	83.298	88.379	91.952	99.607	60
25	26.757	31.264	11	61	36.300	41.303	47.342	60.335	75.514	80.232	84.476	89.591	93.186	100.888	61
17	28.300	32.910	12	62	37.068	42.126	48.226	61.335	76.630	81.381	85.654	90.802	94.419	102.166	62
88	29.819	34.528	13	63	37.838	42.950	49.111	62.335	77.745	82.529	86.830	92.010	95.649	103.442	63
41	31.319	36.123	14	64	38.610	43.776	49.996	63.335	78.860	83.675	88.004	93.217	96.878	104.716	64
78	32.801	37.697	15	65	39.383	44.603	50.883	64.335	79.973	84.821	89.177	94.422	98.105	105.988	65
30	34.267	39.252	16	66	40.158	45.431	51.770	65.335	81.085	85.965	90.349	95.626	99.331	107.258	66
39	35.718	40.790	17	67	40.935	46.261	52.659	66.335	82.197	87.108	91.519	96.828	100.55	108.526	67
35	37.156	42.312	18	68	41.713	47.092	53.548	67.334	83.308	88.250	92.689	98.028	101.78	109.791	68
91	38.582	43.820	19	69	42.494	47.924	54.438	68.334	84.418	89.391	93.856	99.228	103.00	111.055	69
56	39.997	45.315	20	70	43.275	48.758	55.329	69.334	85.527	90.531	95.023	100.43	104.21	112.317	70
12	41.401	46.797	21	71	44.058	49.592	56.221	70.334	86.635	91.670	96.189	101.62	105.43	113.577	71
39	42.796	48.268	22	72	44.843	50.428	57.113	71.334	87.743	92.808	97.353	102.82	106.65	114.835	72
18	44.181	49.728	23	73	45.629	51.265	58.006	72.334	88.850	93.945	98.516	104.01	107.86	116.092	73
30	45.558	51.179	24	74	46.417	52.103	58.900	73.334	89.956	95.081	99.678	105.20	109.07	117.346	74
14	46.928	52.620	25	75	47.206	52.942	59.795	74.334	91.061	96.217	100.84	106.39	110.29	118.599	75
12	48.290	54.052	26	76	47.997	53.782	60.690	75.334	92.166	97.351	102.00	107.58	111.50	119.850	76
33	49.645	55.476	27	77	48.788	54.623	61.586	76.334	93.270	98.484	103.16	108.77	112.70	121.100	77
78	50.993	56.892	28	78	49.582	55.466	62.483	77.334	94.373	99.617	104.32	109.96	113.91	122.348	78
18	52.336	58.301	29	79	50.376	56.309	63.380	78.334	95.476	100.75	105.47	111.14	115.12	123.594	79
12	53.672	59.703	30	80	51.172	57.153	64.278	79.334	96.578	101.88	106.63	112.33	116.32	124.839	80
11	55.003	61.098	31	81	51.969	57.998	65.176	80.334	97.680	103.01	107.78	113.51	117.52	126.082	81
36	56.329	62.487	32	82	52.767	58.845	66.076	81.334	98.780	104.14	108.94	114.69	118.73	127.324	82
16	57.649	63.870	33	83	53.567	59.692	66.976	82.334	99.880	105.27	110.09	115.88	119.93	128.565	83
51	58.964	65.247	34	84	54.368	60.540	67.876	83.334	100.98	106.39	111.24	117.06	121.13	129.804	84
12	60.275	66.619	35	85	55.170	61.389	68.777	84.334	102.08	107.52	112.39	118.24	122.32	131.041	85
19	61.582	67.985	36	86	55.973	62.239	69.679	85.334	103.18	108.65	113.54	119.41	123.52	132.277	86
32	62.884	69.346	37	87	56.777	63.089	70.581	86.334	104.28	109.77	114.69	120.59	124.72	133.512	87
32	64.182	70.703	38	88	57.582	63.941	71.484	87.334	105.37	110.90	115.84	121.77	125.91	134.745	88
38	65.476	72.055	39	89	58.389	64.793	72.387	88.334	106.47	112.02	116.99	122.94	127.11	135.978	89
31	66.766	73.402	40	90	59.196	65.647	73.291	89.334	107.56	113.15	118.14	124.12	128.30	137.208	90
10	68.053	74.745	41	91	60.005	66.501	74.196	90.334	108.66	114.27	119.28	125.29	129.49	138.438	91
16	69.336	76.084	42	92	60.815	67.356	75.101	91.334	109.76	115.39	120.43	126.46	130.68	139.666	92
19	70.616	77.419	43	93	61.625	68.211	76.006	92.334	110.85	116.51	121.57	127.63	131.87	140.893	93
10	71.893	78.750	44	94	62.437	69.068	76.912	93.334	111.94	117.63	122.72	128.80	133.06	142.119	94
17	73.166	80.077	45	95	63.250	69.925	77.818	94.334	113.04	118.75	123.86	129.97	134.25	143.344	95
11	74.437	81.400	46	96	64.063	70.783	78.725	95.334	114.13	119.87	125.00	131.14	135.43	144.567	96
13	75.704	82.720	47	97	64.878	71.642	79.633	96.334	115.22	120.99	126.14	132.31	136.62	145.789	97
13	76.969	84.037	48	98	65.694	72.501	80.541	97.334	116.32	122.11	127.28	133.48	137.80	147.010	98
14	78.231	85.351	49	99	66.510	73.361	81.449	98.334	117.41	123.23	128.42	134.64	138.99	148.230	99
14	79.490	86.661	50	100	67.328	74.222	82.358	99.334	118.50	124.34	129.56	135.81	140.17	149.449	100

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 sample (contd)

n	δ	0.2
22	0.0	.19343
	0.5	.19843
	1.0	.20616
23	0.0	.19001
	0.5	.19472
	1.0	.20197
24	0.0	.18677
	0.5	.19121
	1.0	.19804
25	0.0	.18370
	0.5	.18790
	1.0	.19433
26	0.0	.18077
	0.5	.18476
	1.0	.19084
27	0.0	.17799
	0.5	.18178
	1.0	.18753
28	0.0	.17533
	0.5	.17894
	1.0	.18440
29	0.0	.17280
	0.5	.17624
	1.0	.18142
30	0.0	.17037
	0.5	.17365
	1.0	.17859
31	0.0	.16805
	0.5	.17119
	1.0	.17589
32	0.0	.16582
	0.5	.16882
	1.0	.17332
33	0.0	.16368
	0.5	.16656
	1.0	.17086
34	0.0	.16162
	0.5	.16439
	1.0	.16850
35	0.0	.15964
	0.5	.16230
	1.0	.16625
36	0.0	.15774
	0.5	.16029
	1.0	.16408
37	0.0	.15590
	0.5	.15836
	1.0	.16200
38	0.0	.15413
	0.5	.15650
	1.0	.16000
39	0.0	.15242
	0.5	.15471
	1.0	.15808
40	0.0	.15076
	0.5	.15297
	1.0	.15622

ected one-
ov statistic

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

		α						
.02	.01	<i>n</i>	δ	.2	.1	.05	.02	.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
1732	.52519		1.0	.18753	.21676	.24267	.27330	.29439
1922	.43071	28	0.0	.17533	.20283	.22721	.25600	.27582
404	.45776		0.5	.17894	.20712	.23208	.26156	.28185
1067	.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
1516	.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