UNIVERSITY OF ESWATINI
DEPARTMENT OF CHEMISTRY

MAIN EXAMINATION 2020/2021

TITLE OF PAPER:	RESEARCH METHODS IN CHEMISTRY
COURSE NUMBER:	CHE 604
TIME ALLOWED:	THREE (3) HOURS
INSTRUCTIONS:	ANSWER ANY FOUR (4) QUESTIONS

Special Requirements

1. Data sheet.
2. Graph Paper

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

QUESTION 1 [25]

(a) Briefly discuss the technique "Analysis of Variance" and why would such a research method be useful in data analysis (6)

(b) (i) Use a diagram to explain what is meant by aliasing? (3)

(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 2 [25]

(a) (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)

(b) What is meant by a "reference method" in the analytical chemistry laboratory? (2)

(c) A new GC-MS method for the analysis of DDT in tissue samples is being evaluated by comparing the results obtained using it with that of the reference method based on HPLC. The results of the concentrations of DDT (in ppb), by the two methods are as shown in the table below:

Method	DDT concentration, ppb								
HPLC Reference	2.16	2.42	2.16	2.35	2.31	2.43			
New GC-MS	2.15	2.23	2.15	2.13	3.01	2.46	2.21	2.36	2.31

(i) Would you consider the value "3.01" in the data obtained by the new GC-MS method an "outliar" (3)

(ii) Is there a significant difference between the two methods at the 95% confidence level. (5)

(iii) Comment on the precision of the new GC-MS method relative to the reference one at 95% confidence level. (3)

(d) In chemical research, the encoding and decoding of analytical information affects the accuracy and precision of research data. Use diagrams to explain how the Si-VIDICON image sensor works in decoding analytical information. (5)

QUESTION 3 [25]

(a) (i) Write down the equation that describes the "normal curve of error" in chemometrics, and explain all terms appearing in it. (4)

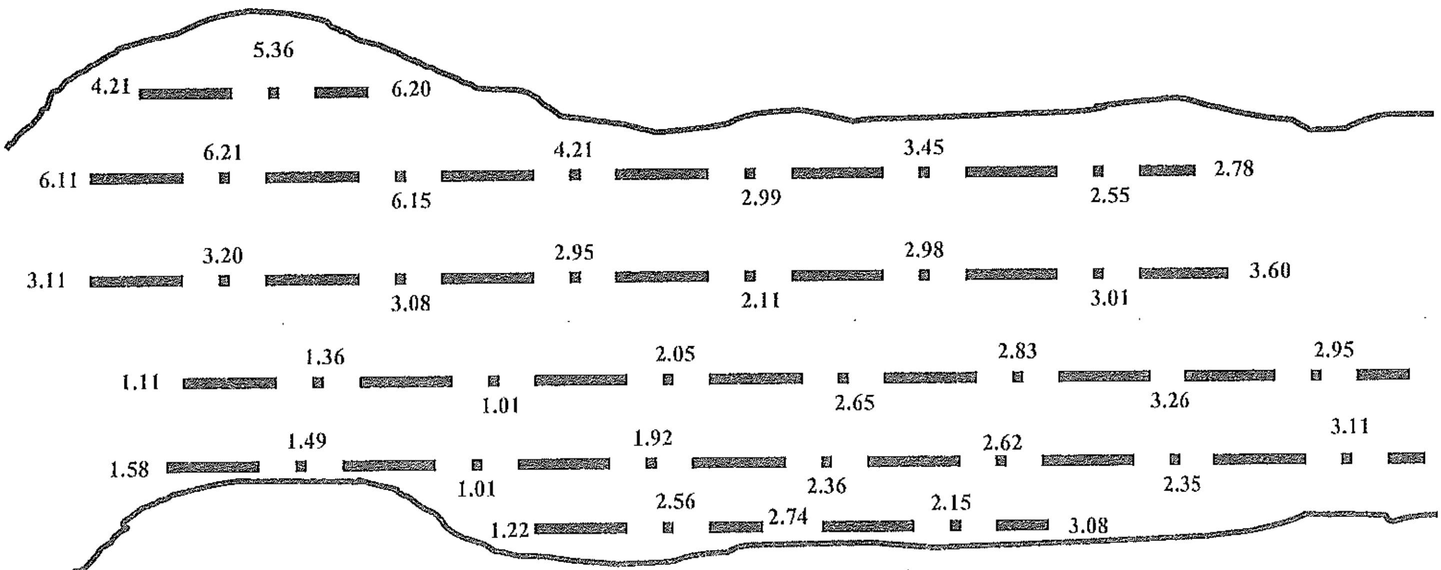
(ii) Under what conditions in analytical sampling will the sample variance be the same as the population variance (2)

(b) The following absorbance data was obtained in triplicate during a standard additions determination of zinc in a river sediment 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 μL, 5μ L, 10 μL, and 15 μL of a 100 ppm Zn standard solution was added to 10-mL aliquots of sample, respectively.

Thirty six (36) samples of river sediment were taken from a river 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. The spatial distribution of zinc was found to be as follows:



(i) Identify the hotspot and coldspot in this population (3)

(ii) Use the Kolmogorv-Smirnoff test to show that the distribution of zinc in the field is not Gaussian. (7)

(iii) Calculate the uncertainty due to the sampling operation in ppm units, if five (5) portions of certified reference material gave the following results: **5.22 5.21 5.35 5.20 5.23** (4)

(iv) 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 4 [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? (2)

(iv) Give the operational definition of "detection limit". (3)

(b) What is the difference between "White Noise" and "Fundamental Noise" in analytical instrumentation. (3)

(c) In regard to Johnson Noise,

(i) Explain it 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 (3)

(d) In regard to Shot Noise,

(i) Explain it 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 5 [25]

(a) (i) What is meant by a "certified reference material" in the analytical laboratory (2)

(ii) 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? (2)

(ii) Explain how blind samples are used to evaluate validity and reliability of Hg 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 DDT in a tissue sample:

Day #	1	2	3	4	5	6	7	8	9	10
DDT, ppb	10	11	10	9	21	10	11	5	4	10

(i) What is meant by an "in-house reference material"? (3)

(ii) Draw the quality control chart for the DDT determination, assuming that the in-house reference material is 10±2 ppb DDT. 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)

QUESTION 6 [25]

(a) In the analysis of Cu in agricultural soils by flame atomic absorption spectrophotometry, describe three (3) sources of error in the analytical results. (6)

(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 populations (4)

(e) Describe Visman's approach to sampling coal in a moving belt. (4)

(f) Although amplification does not eliminate noise, amplifiers are useful in analytical data acquisition. For the integrator operational amplifier, draw the circuit and describe the output using the relevant equation. (3)

APPENDIX 2

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	0.6579
0.5	0.6915	0.6950	0.6965	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

z	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

Value of t for a confidence interval of / *Critical value of |t| for P values of number of degrees of freedom*	90% / 0.10	95% / 0.05	98% / 0.02	99% / 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 ($P = 0.05$)

ν_2 \ ν_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	245.9
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

ν_1 = number of degrees of freedom of the numerator and ν_2 = number of degrees of freedom of denominator.

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

ν_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 ν_2 = number of degrees of freedom of the minator.

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

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

TABLE B Critical values of Student's t-distribution

ν \ α	0.9	0.5	0.4	0.2	0.1	0.05	0.02	0.01	0.001	α / ν
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	∞

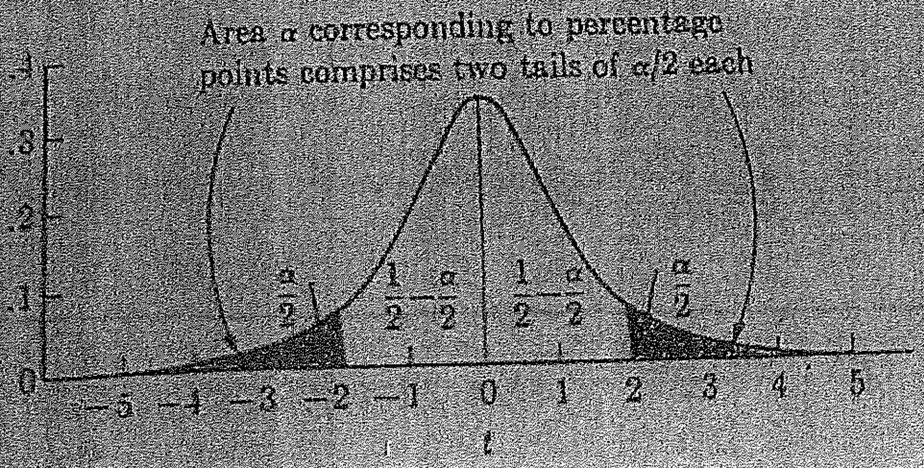


TABLE D Critical values of the chi-square distribution

ν \ α	.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