

— Contents —

| | | |
|----------------|--|-------------|
| Preface | | viii |
| 1 | What is statistics? | 1 |
| 2 | Describing a set of data | 5 |
| 2.1 | Introduction | 5 |
| 2.2 | Describing a small set of data | 5 |
| 2.3 | Describing a large set of data | 9 |
| 2.4 | The normal distribution | 11 |
| 2.5 | Other distributions | 14 |
| 2.6 | Summary | 16 |
| | Problems | 17 |
| 3 | Errors and repeatability | 18 |
| 3.1 | Introduction | 18 |
| 3.2 | Error bias and precision | 18 |
| 3.3 | Propagation of errors | 22 |
| 3.4 | Repeatability | 28 |
| 3.5 | Summary | 31 |
| | Problems | 31 |
| 4 | Fixed bias – detection, estimation and correction | 33 |
| 4.1 | Introduction | 33 |
| 4.2 | Detection of a fixed bias | 33 |
| 4.3 | Estimating the magnitude of bias | 38 |
| 4.4 | The sample size needed to estimate bias | 41 |
| 4.5 | Correction of fixed bias | 42 |
| 4.6 | Repeatability again | 44 |
| 4.7 | Summary | 44 |
| | Problems | 45 |

| | | |
|----------|---|------------|
| 5 | Relative bias – detection, estimation and correction | 48 |
| 5.1 | Introduction | 48 |
| 5.2 | Is the bias fixed or relative? | 48 |
| 5.3 | Fitting the ‘best’ straight line | 49 |
| 5.4 | Fitting the ‘best’ straight line through the origin | 56 |
| 5.5 | Correction of relative bias | 59 |
| 5.6 | Correlation and percentage fit | 60 |
| 5.7 | Correlated errors | 61 |
| 5.8 | Summary | 62 |
| | Problems | 63 |
| 6 | Precision | 65 |
| 6.1 | Introduction | 65 |
| 6.2 | Estimating precision | 65 |
| 6.3 | The number of determinations needed to estimate precision | 69 |
| 6.4 | Is Jones less precise than the other analysts? | 70 |
| 6.5 | Combining standard deviations | 71 |
| 6.6 | Is the new operator acceptable? | 72 |
| 6.7 | The number of determinations needed to compare two analytical methods | 73 |
| 6.8 | Is the precision of the method related to the concentration? | 74 |
| 6.9 | Summary | 77 |
| | Problems | 77 |
| 7 | Calibration | 79 |
| 7.1 | Introduction | 79 |
| 7.2 | Fitting a calibration line | 80 |
| 7.3 | Estimating the concentration of an unknown sample | 83 |
| 7.4 | Increasing the size of the calibration experiment | 85 |
| 7.5 | An external estimate of error standard deviation | 86 |
| 7.6 | Repeat determinations on the unknown sample | 88 |
| 7.7 | Simulation of a calibration experiment | 88 |
| 7.8 | A calibration line through the origin | 90 |
| 7.9 | Correcting for bias in calibration | 93 |
| 7.10 | Summary | 96 |
| | Problems | 96 |
| 8 | Calibration – further difficulties | 100 |
| 8.1 | Introduction | 100 |
| 8.2 | Weighted regression | 100 |
| 8.3 | Confidence interval with weighted regression | 105 |
| 8.4 | Simulation of a calibration experiment | 106 |
| 8.5 | Calibration curves | 110 |
| 8.6 | Detecting curvature | 118 |

| | | |
|-----------|--|------------|
| 8.7 | Summary | 123 |
| | Problems | 124 |
| 9 | Reproducibility (1) | 126 |
| 9.1 | Introduction | 126 |
| 9.2 | A precision experiment | 126 |
| 9.3 | Variability between and within laboratories | 126 |
| 9.4 | The analysis of variance table | 130 |
| 9.5 | Variance estimates and their significance | 134 |
| 9.6 | Assumptions underlying analysis of variance | 140 |
| 9.7 | Reproducibility | 142 |
| 9.8 | Summary | 144 |
| | Problems | 144 |
| 10 | Reproducibility (2) | 149 |
| 10.1 | Introduction | 149 |
| 10.2 | Analysing all four levels simultaneously | 149 |
| 10.3 | Two-way analysis of variance | 152 |
| 10.4 | Assumptions underlying two-way analysis | 156 |
| 10.5 | Estimating reproducibility | 159 |
| 10.6 | Summary | 161 |
| | Problems | 161 |
| 11 | Various experiments | 163 |
| 11.1 | Introduction | 163 |
| 11.2 | Experiment One | 163 |
| 11.3 | Experiment Two | 167 |
| 11.4 | Experiment Three | 168 |
| 11.5 | Experiment Four | 171 |
| 11.6 | Summary | 176 |
| | Problems | 176 |
| 12 | Precision experiments – advisory publications | 178 |
| 12.1 | Introduction | 178 |
| 12.2 | BS 5497 – organization of the precision experiment | 178 |
| 12.3 | BS 5497 – data analysis | 180 |
| 12.4 | BS 5497 and IS 4259 – points of difference | 183 |
| 12.5 | IS 4259 – data analysis | 185 |
| 12.6 | IS 4259 – design of the precision experiment | 194 |
| 12.7 | Youden and Steiner | 195 |
| 12.8 | Summary | 197 |
| 13 | Miscellaneous topics | 198 |
| 13.1 | Introduction | 198 |

| | | |
|--|---|------------|
| 13.2 | The method of standard additions | 198 |
| 13.3 | Limit of detection | 201 |
| 13.4 | Summary | 204 |
| Appendix 1 The sigma (Σ) notation | | 206 |
| Appendix 2 Nomenclature and formulae | | 207 |
| Solutions to problems | | 211 |
| Bibliography | | 237 |
| Statistical tables | | 238 |
| Table A | The normal distribution | 239 |
| Table B | Critical values for the <i>t</i> -test | 240 |
| Table C | Critical values for the <i>F</i> -test | 241 |
| Table D | Critical values of the product-moment correlation coefficient | 245 |
| Table E | Critical values for the chi-squared test | 246 |
| Table F | Confidence intervals for a population standard deviation | 247 |
| Table G | Critical values for Dixon's test | 248 |
| Table H | Critical values for Cochran's test | 249 |
| Index | | 251 |