Index

543.072 MIL

absorbance, 10, 11, 30, 34, 127 acceptable quality level (AQL), 102 - 3acceptance sampling, 102-3, 106 accreditation, 104 accuracy, 5, 112, 144 action lines, in control charts, 80 - 7additive factors, in experimental design, 192 adjusted coefficient of determination, see coefficient of determination aerosols. 23 albumin, serum, determination, 1, 11, 23 aliases, 204 alternating variable search, 208-10.217 alternative hypothesis, 65-6 American Society for Testing and Materials (ASTM), 7 analysis of variance (ANOVA). 52-9, 76-7, 95, 96, 102, 105, 171, 187, 193–8, 201, 261–3 arithmetic of calculations, 56-9 assumptions, 59 between-block variation in, 189-90 between-column variation in, 195 - 7between-row variation in, 195-7 between-sample variation in, 55-6, 76-7, 91

between-treatment variation in. 189-90 correction term, 195 for comparison of several means, 53-6 in regression calculations, 141 - 8least significant difference in, 56 mean-squares in, 55, 141 one-way, 53-9, 91, 95-8 residual mean square in, 190 - 2robust, 179-80 significant differences in, 58 sums of squares in, 57-8, 141, 190-2, 195-7 total variation in, 56-7 two-way, 97, 189-92, 193-8 within-sample variation in. 76-7,91 antibiotics, 231 antibody concentrations in serum, 23-4 arithmetic mean, see mean assigned value in proficiency testing schemes, 92 assumptions, in linear calibration calculations, 113-14, 134 astigmatism, 10 atomic absorption spectrometry, 9, 11, 142, 148, 216 atomic weights, 99 automatic analysis, 111-13, 216, 221 average run length, 86-9

background signal, see blank Bayesian statistics, 66-9 between-run precision, 6, 105 between-sample variation in ANOVA, see ANOVA bias, 4, 9, 10, 45, 96-8, 99, 104-5 binomial distribution, 156 binomial theorem, 160-1 biweight, 181 blank, 8, 113, 121, 125-6 blocks, 55, 188-92 blood glucose, 91 blood serum, 9 bootstrap, 181-3 boron, 1, 2 bottom-up method for uncertainty, 98-100 box-and-whisker plot, 158 breakdown point, 175, 180 **British Standards Institution** (BSI), 7 bulk sampling, 75, 91 buoyancy effects in weighing, 8 burette, 7, 8 calculators, 13, 18-19 calibration methods, 3, 8, 10, 12, 14, 105, 112-50, 160 canonical variate analysis, 235 censoring of values in collaborative trials, 96 central limit theorem, 26, 154 centrifugal analysers, 216 centroid, of points in calibration

plots, 114, 118, 123



Index

Certified Reference Materials (CRMs), 11, 92 chemometrics, 13-14, 188 chi-squared test, 59-61, 169-71, 261-2, 268 chromium, in serum, determination, 9, 10, 11 clinical analysis, 69, 91, 105, 216.221 cluster, 222 cluster analysis, 228-31, 247 hierarchical, 231 Cochran's test, 95, 272 coefficient of determination, 142-8, 242 adjusted, 142-8, 242 robust, 181 coefficient of variation (CV), see relative standard deviation collaborative trials, see method performance studies colorimetry, 11, 216 colour blindness, 10 comparison of analytical methods, using regression, 130-5 comparison of experimental result with standard value, 2, 38-9, 160-1, 164, 261-2 of means of several sets of data, 53-6, 261-2 of means of two sets of data, 39-43, 261-2 of paired data, 43-5, 164-5, 261 - 2of standard deviations of two sets of data, 47-9, 261-2 complete factorial design, 198-203, 211-13 concentration determination by calibration methods, 121-4, 128-9, 137-9 confidence interval of the mean, 26-8, 30-1 confidence limits of the mean, 26-8, 29, 30-1, 77-8, 79-80, 182-3 in linear calibration plots, 113, 120, 122, 123-4, 131-4, 138-9, 140 confidence limits of the median. 156 confounding, 43, 204

confusion matrix, 233 consensus value, in proficiency testing schemes, 92 contour diagrams, 208-13, 216 control charts, see Shewhart charts, cusum charts, zone control charts controlled factor, 53, 76, 187, 191, 197 Cook's squared distance, 150 correction term in ANOVA, see ANOVA correlation, 13 correlation coefficient, see product-moment correlation coefficient and Spearman's rank correlation coefficient correlation matrix. 222-4 covariance, 114, 225 covariance matrix, 225-6 coverage factor, 98 critical values in statistical tests, 38-9, 46, 47-9, 95 cross-classified designs, 193 cross-validation, 233-4, 238-40, 244 cubic splines, 148 cumulative distribution function, 63-5 cumulative frequency, 61-3 curve. 61-2 curve-fitting, 141-9, 162, 175, 183 curvilinear regression, see regression, curvilinear cusum (cumulative sum) chart, 86-90

data vector, 222 databases, 14, 69 decision rule, 233 degrees of freedom, 28, 40, 55, 56, 60, 117, 119, 120, 122, 123, 124, 134, 140, 147, 170, 190-2, 195-7, 205 dendrogram, 229-31 discriminant analysis, 231-5 disjoint class modelling, 236-7 distance function, 177, 179 distribution-free methods, see nonparametric methods distribution of repeated measurements, 19-23

Dixon's Q, 51-2, 176, 179, 261-2.268 dot plot, 4, 5, 51-2, 54, 56, 156-7 down-weighting of data, 155, 175 draftsman plot, 223-4 dummy factors, 204-5

eigenvalue, 225, 242 eigenvector, 225 electrochemical analysis methods, 110, 128 emission spectrometry, 110, 128 environmental analysis, 111, 159 enzymatic analysis, 12, 206-8 error bars, 135-6 errors, see gross, random and systematic errors errors in significance tests, 65-6 Euclidian distance, 228-31, 235-6 Eurachem/CITAC, 99 Excel, see Microsoft Excel expanded uncertainty, 98-102 expected frequency, in chi-squared test, 60-1 experimental design, 10, 12, 94, 186-205 exploratory data analysis (EDA), see initial data analysis (IDA) exponential functions in curve-fitting, 141

F-test, 30, 47-9, 55, 57, 59, 66, 98, 141, 168, 192, 202, 205, 261-2, 266-7 factorial designs, 198-205 factors affecting experimental results, 12, 13, 94-5, 106, 187 fences, 158 Fibonacci series, 208 Fisher, R. A., 189 fitted y-values, 119 fitness for purpose, 106 five-number summary, 158 fixed-effect factors, see controlled factors fluorescence spectrometry, 33, 53-6, 142, 187, 188, 221, 245 food and drink analysis, 91 forensic analysis, 1, 69, 91, 145



Fourier transform methods, 228, 245 fractional factorial designs, 95, 106, 203–5 frequency, in chi-squared test, 59–61 frequency table, 19 Friedman's test, 170, 261–2 functional relationship by maximum likelihood method (FREML), 134–5

gas-liquid chromatography, 148, 216, 221, 231 Gaussian distribution, *see* normal distribution generating vector, in Plackett-Burman designs, 205 genetic algorithms, 245–6 geometric mean, 24, 30–1 confidence interval of, 31 goodness-of-fit, 59–65, 243 gravimetric analysis, 8 gross errors, 3, 155 Grubbs' test, 49–52, 96, 149, 176, 261–2, 267

Half-factorial designs, 203-4 Heavy-tailed distributions, 155, 175 heteroscedasticity, 134, 135 hierarchical designs, 193 high-performance liquid chromatography, 187 histogram, 19-20, 159, 182-3 hollow-cathode lamp, 142 homogeneity of samples in proficiency testing, 91 homogeneity of variance, 59 homoscedasticity, 134, 135 Horwitz trumpet, 92–3, 98 Huber's robust estimation methods, 177-9

immunoassay, 11, 142, 145, 148 incomplete factorial design, *see* fractional factorial design indicator errors, 8 influence function, 150 initial data analysis (IDA), 4, 148–9, 155–60 inner-filter effects, in fluorimetry, 145 intelligent instruments, 10, 111 interactions between factors, 13, 95, 192, 193-8, 200-5, 209-13 intercept, of linear calibration graph, 113, 114, 118-24, 127, 128, 130-1, 136-8, 173-5, 180-1 internal quality control (IQC) standard, 79 inter-quartile range, 92, 156, 158, 177 International Organisation for Standardization (ISO), 5, 49, 90, 92, 121, 124 International Union of Pure and Applied Chemistry (IUPAC), 25, 99 intersection of two straight lines, 140-1 inverse calibration, 238-40, 246 iron in sea-water, determination, 9 iterative methods. 175-6 iterative univariate method. see alternating variable search iteratively weighted least squares, 181

J-charts, see zone control charts

Kendall, 172 *k*-means method, 231 K-nearest neighbour (KNN) method, 235–6 knots, in spline functions, 148 Kolmogorov-Smirnov methods, 63–5, 261–2, 271 Kruskal-Wallis test, 169, 261–2

laboratory information management systems (LIMS), 14 latent variables, 227 Latin squares, 192–3 learning objects, 232 least median of squares (LMS), 180–1 least significant difference, in ANOVA, 56 least-squares method, 14, 117, 118–19, 141, 174, 180, 181 'leave-one-out method', 233, 244

levels of experimental factors, 12, 94, 106, 187 LGC, 11 limit of decision, 125 limit of detection, 3, 105, 113, 124-7, 135, 139 limit of determination, 105, 126 limit of quantitation, 105, 126 line of regression of x on y, 118 line of regression of y on x, 118-27 linear discriminant analysis, 232-5, 247 linear discriminant function, 232 logarithmic functions in curvefitting, 141 logit transformation, 145 log-log transformation, 145 log-normal distribution, 23-4, 30-1, 52, 155, 175 lower quartile, 156, 158 Mann-Whitney U-test, 166-7, 168, 183, 261-2, 270 masking, in outlier tests, 52 mass spectrometry, 110 matched pairs, 96-8 MATLAB[®], 246–7 matrix effects, 127-8, 130 matrix matching, 128 mean, 13, 17-23, 25-8, 29, 49, 79, 176-7 mean square, in ANOVA, 202 mean squares, in nonlinear regression, 146-8 measurement variance, 76 measures of location, 17 measures of spread (dispersion), 17 median, 49, 92, 149, 155-62, 164, 169-71, 173-5, 178, 181 median absolute deviation (MAD), 177-9, 181 method of standard additions. see standard additions method performance studies, 11, 94-8, 108, 183 method transfer, 104 method validation, 104-6, 129, 130 methyl orange, indicator error due to, 8



Index

Microsoft Excel[®], 14, 23, 39, 41, 42. 49. 58. 77. 84-5. 131-3. 140, 141-2, 143, 182, 194, 201 Minitab®, 14, 23, 39, 42-3, 58, 63, 65, 85-6, 89-90, 121, 135, 143, 156, 159, 170-1, 175. 179. 182. 194-5. 205. 22-6, 230-1, 233-5, 238-40, 241-3, 244 modified simplex optimization methods, 214-15 molar absorptivity, 10 monochromators, systematic errors due to, 9, 10 multiple correlation coefficient, see coefficient of determination multiple regression, see regression multivariate ANOVA (MANOVA), 222 multivariate calibration, 132, 183 multivariate methods, 221-47 multivariate regression, see regression

National Institute for Science and Technology (NIST), 11 National Physical Laboratory (NPL), 11 natural computation, 216-17, 245 - 7near-IR spectroscopy, 217, 235 nebulisers, 23 nested designs, 193 neural networks, 245-7 non-parametric methods, 14, 119, 150, 154-75, 180, 183-4, 261-2 normal distribution, 20-3, 26-7, 31, 45, 47, 52, 59, 61-5, 68, 85, 92, 113-14, 125-6, 142, 154-5, 160, 162, 163, 164, 175, 187, 198, 237, 264-5 tests for, 61-5 normal probability paper, 61-3, 121 nuclear magnetic resonance spectroscopy, 217, 235 null hypothesis, 38, 39, 43-4, 47, 49, 51, 55, 59, 64, 65-6, 67, 95, 105, 117–18, 161, 162, 163, 164, 165, 166, 167, 168, 170, 171, 172, 183, 239–40 number bias, 10

observed frequency, in chi-squared test, 60-1 one-at-a-time experimental designs and optimisation, 198 one-sided test, 41-2, 45-6, 48-9, 55, 164, 166 one-tailed test. see one-sided test one-way analysis of variance (ANOVA), see analysis of variance optimisation, 12, 13, 111, 197, 198, 206-17 orthogonality, 224 outliers, 2, 49-52, 92, 95, 98, 149-50, 155, 156, 157, 175-9, 261-2 in regression, 149-50, 172, 174

P-values. 38 paired alternate ranking, 168 paired data, 43, 164, 170 paired t-test, 43-5, 105, 132, 161, 164, 261-2 partial least squares regression, see regression. particle size analysis, 2 path-length, 10 pattern recognition, 231-2 periodicity, effects in sampling, 75 of + and - signs, 163 personal computers, 10, 13-14, 111, 139, 155, 156, 160, 175, 182-4 pipette, 7, 8 Plackett-Burman designs, 204-5 plasma spectrometry, 11, 128, 216 polynomial equations in curve fitting, 141, 146-8 pooled estimate of standard deviation, 40, 42, 66, 140 population 20, 30, 75 posterior distribution, 67-9 power of a statistical test, 66, 162, 183 precision, 4, 29, 49, 95, 105, 112

predicted residual error sum of squares (PRESS), 239-40, 242-3. 244-5 presentation of results, 29-30 principal component, 224 principal component analysis, 224-8.235 prior distribution, 67-8 principal component regression, see regression process analysis, 111, 221 process capability, 79, 82-6 process mean, 80 product-moment correlation coefficient, 114-18, 130, 133-4, 142, 172, 222-4 proficiency testing schemes, 11, 12, 91-4, 100, 106 propagation of random errors, 31 - 4propagation of systematic errors, 34-5 proportional effects, in standard additions, 128 pseudo-values, 178

Q-test for outliers, *see* Dixon's Q quadratic discriminant analysis, 233 qualitative analysis, 1 qualitative factors, 187 quality, 74 quality control, 78–90 quantitative analysis, 1, 2–3 quantitative factors, 187 quantitative structure activity relationships (QSAR), 217 quartiles, 156, 158

radiochemical analysis methods, 110 random-effect factors, 53, 76, 187, 188 random errors, 3–13, 25–6, 35, 47–9, 78, 96–8, 99, 119, 198 in regression calculations, 113–14, 119–21, 130–1, 134–5, 138–9, 140, 145 random number table, 75, 188, 268 random sample, 75 randomisation, 59, 188–9 randomised block design, 189



range, 81-6, 89-90, 95 rank correlation, see Spearman's rank correlation coefficient ranking methods, 162-5, 168, 169-72 recovery, 105 rectangular distribution, 99 regression methods, 110-50, 172-5, 180-1, 237-45 assumptions used in, 113-14, 134 curvilinear, 13, 113, 116-17, 142-9, 163 for comparing analytical methods, 105, 261-2 linear, 13, 45, 110-42, 162, 163, 171-5, 180-1 multiple, 228, 238-40, 241, 245, 247 multivariate, 237-45 nonparametric, 150, 172-5 partial least squares, 243-5, 247 principal component, 241-3, 245, 247 robust, 150, 180-1 relative errors, 19, 32-3, 35 relative standard deviation (RSD), 8, 19, 32-3, 34 repeatability, 3, 5, 6, 81, 95, 105 replicates, in experimental design, 194 reproducibility, 5, 6, 91, 95, 101, 105 re-sampling statistics, 181-8 re-scaled sum of z-scores, 93 residual diagnostics, 121, 239-40 residuals, in regression calculations, see y-residuals resolution, of experimental designs, 204 response surface designs, 202 response surfaces, in optimisation, 208-16 robust ANOVA, 179-80 robust mean, 177-9 robust methods, 49, 52, 92, 149, 150, 155, 175-81, 183-4 robust regression, 180-1 robust standard deviation, 177-9 rotational effects, in standard additions, 128 rounding of results, 29-30 ruggedness test, 94-5, 106

runs of + and – signs, 143–8, 162–3 Ryan-Joiner test for normality, 63

sample, 20, 24-5, 30, 75 sampling, 9, 75-8 sampling distribution of the mean, 25-6, 55, 102-3 sampling uncertainty, 78 sampling variance, 76, 78 sampling with replacement, 181-3 SAS[®], 225 scatter diagrams, 223 score plots, 226 screening designs, 198 seed points, 231 selectivity, 12 sensitivity, 12, 126-7 sensors, 235 sequences of + and - signs, see runs of + and - signs sequential use of significance tests, 66 Shewhart chart, 79-87, 89, 124 Siegel-Tukey test, 159, 168, 261-2, 270 sign test, 160-2, 261-2, 269 signed rank test, see Wilcoxon signed rank test significance levels, 38 significance tests, 37-69, 105, 160 comparing two means, 39-43 comparing two variances, 47–9 conclusions from, 65-6 for correlation coefficient, 117 on mean, 37-9 problems in sequential use, 66 significant figures, 29 **SIMCA**, 237 similarity in cluster analysis, 229 simplex optimisation, 213-16, 217 simulated annealing, 216-17, 245 single linkage method, 229 single point calibration, 121 skewness, 182 slope of linear calibration graph, 113, 114, 118-24, 127, 128, 130-1, 136-8, 173-5, 180-1 software. 13-14 soil samples, 1, 2, 105

Spearman's rank correlation coefficient, 171-2, 271 speciation problems, 131 specimen, 25 spectrometer, 11 spiking, 105, 128-9 spline functions, 148 spreadsheets, 14, 121 standard additions method, 113, 127-30 standard deviation, 13, 17-19, 29, 34, 38, 39, 47-9, 79, 84-5, 98, 105, 176-7 of slope and intercept of linear calibration plot, 119-20 standard error of the mean (s.e.m.), 25, 29 standard flask, 7-8 standard normal cumulative distribution function. 22-3, 63-5, 264-5 standard normal variable, 22, 92-3 standard reference materials, 3, 11, 12, 79, 104–5, 124 standard uncertainty, 98-102 standardisation, 22, 227, 228, 235 standardised median absolute deviation (SMAD), 177, 180 standardised normal variable (z), 22 steel samples, 1, 3 steepest ascent, optimisation method, 210-13 stem-and-leaf diagram, 159 sum of squared z-scores, 93 sums of squares, in nonlinear regression, 141-7 suspect values, see outliers systematic errors, 3-12, 20, 25-6, 30, 31, 35, 37-9, 87, 96-8, 99, 101, 111, 131, 188 t-statistic, 28, 38-9, 40, 41, 42, 56, 60, 66, 117-18, 120, 122, 123, 124, 140, 205, 239-40, 242-3, 266 t-test, 30, 47, 48, 157, 160, 183, 261 - 2target value, 92 in control charts, 80, 87 temperature effects in volumetric analysis, 7-8



test extract, 25 test increment, 75, 77-8 test set, 233, 247 test solution, 25 Theil's methods for regression lines, 172-5, 180 thermal analysis methods, 110 tied ranks, 165 titrimetric analysis, 2-9, 33 tolerances, of glassware and weights, 7 tolerance quality level (TQL), 102 - 3top-down method for uncertainty, 100-1 training objects, 232 training set, 233, 247 transformations, in regression, 145 translational effects, in standard additions, 130 treatments, 189-92 trend, significance test for, 161 - 2triangular distribution, 99 trimming, 176, 178, 180 trueness, 4, 104-5 Tukey's quick test, 167-8, 261-2 two-sample method, see Youden matched pairs method two-sided test, 41-2, 45-6, 48-9, 117, 162, 164 two-tailed test, see two-sided test

two-way ANOVA, *see* ANOVA type I errors, in significance tests, 65–6, 125 type II errors, in significance tests, 65–6, 125 type A uncertainties, 98–100 type B uncertainties, 98–100 unbiased estimators, 20 uncertainty, 6, 29, 35, 92, 98–102, 106 uncontrolled factor, *see* random

effect factor uniform distribution, 99 univariate methods in optimisation, 206–8 unweighted regression methods, 114, 122–3 upper quartile, 156, 158 Unscrambler[®], The, 14, 225, 241, 244 UV-visible spectroscopy, 217

V-mask, 88–89 Vamstat[®], 14 validation, *see* method validation variance, 19, 32, 41, 47–9, 97–8, 205 volumetric glassware, 7

Wald-Wolfowitz runs test, 162–3, 269

warning lines, in control charts, 80-7 water analysis, 91 weighing, 7, 8, 10, 34 bottle, 7-8 buoyancy effects in, 8 by difference, 7, 10, 99-100 weighted centroid, 136-9 weighted regression methods, 114, 134, 135-9, 145, 181 weights, of points in weighted regression, 135-9 Wilcoxon signed rank test, 163-5, 261-2.270 winsorisation, 176-9, 180 within-run precision, 6, 105 within-sample variation, 54-5 word-processors, 13

X-ray crystallography, 217

y-residuals, in calibration plots, 118, 119–20, 142–8, 149–50, 180–1 standardised, 149–50 Yates's algorithm, 201 Yates's correction, 60–1 Youden matched pairs method, 96–8, 106

z-scores, 91–3 z-values, 22–3, 63–5, 103 zone control charts, 89–90