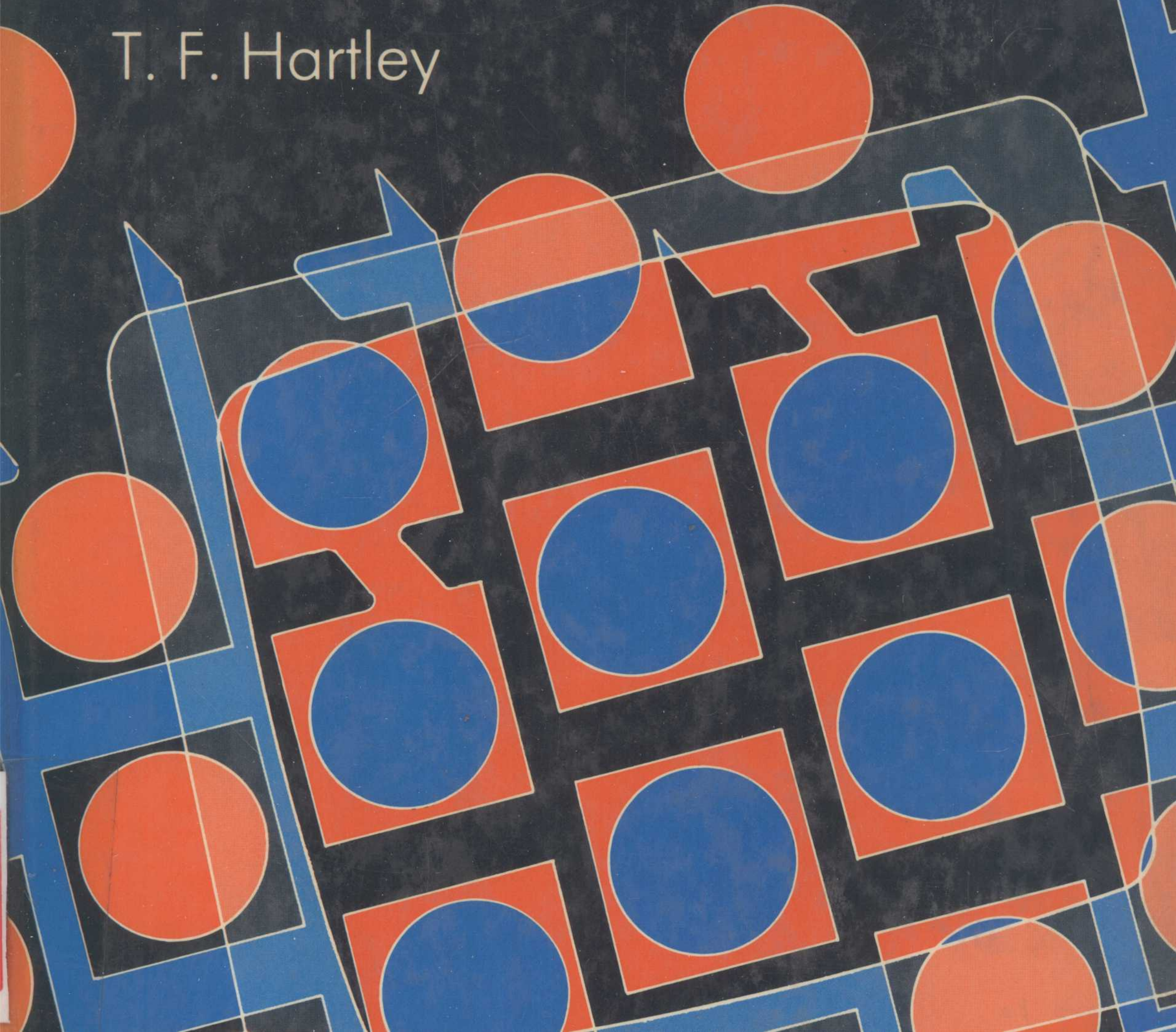
Ellis Horwood Series in ANALYTICAL CHEMISTRY

COMPUTERIZED QUALITY CONTROL

Programs for the analytical laboratory

T. F. Hartley



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T. F. Hartley

Introduction

Every analytical chemist would like to believe that the data reported from their laboratory are of a uniform and sustained quality. However, it is inevitable that from time to time doubt about some of the batches creeps in. The reasons for such doubts can originate from a number of sources. One may be that the usual method has been used to analyse a batch of specimens with a matrix that was slightly different from that for which the method was optimized. Consequently there is a real possibility that there may be a constant or systematic bias throughout the data reported for those samples. Will this possible bias affect the customer's perception of what the results mean? Another more common suspicion is that the instrumentation is either not operating or being operated exactly as intended. There are other examples, so clearly there is a need for some objective assistance in this sensitive and critical area of the perceived versus the actual analytical performance of the laboratory.

In this book I have aimed to outline automated statistical techniques that can provide this type of assistance without making unreasonable demands on the analyst's valuable time. These methods are all based on well accepted quality control procedures that can be run easily as BASIC computer programs on a personal computer or computer terminal in the laboratory. In addition I have included computerized procedures to assist the analyst with the selection of analytical performance criteria that will ensure that their customers are provided with results at the level of accuracy and precision that they require.

The approach has been from the point of view of a practising analyst who would prefer to be provided with the essential information required, with the option to follow up the full theoretical details when convenient. For this reason the bibliography and references extend beyond those items cited specifically in the text. The reader is urged to study all the titles in that section and decide which of those would be particularly relevant to their organization's activities. One feature that may be noticed while consulting the Bibliography covers a considerable time span; from 1940 to the present. It would appear that although most statistical quality control techniques were developed some years ago it has taken some time for them to be implemented on an extensive basis in analytical laboratories. This is a reflection of a common attitude to quality control which is that it is tedious and therefore only the minimum necessary will be put into everyday use. It is to be hoped that computerized quality control will shield the user from the tedium, encourage analysts to adopt more than just the minimum and eventually extend their interest to the more sophisticated techniques available.

The programs have all been written in Personal BASIC, (Digital Research). They were developed on a concurrent CPM–86 v. 3.1 computer (Labtam 3000) with a 132 column dot matrix printer. (Two programs require more than 80 columns to accommodate the printout conveniently but these could be adapted to an 80 column format if necessary.) The BASIC words actually used are listed below; it will be evident that no uncommon features of the language have been implemented

ABS	AND	CLOSE	DIM	ELSE	EXP
FOR	GOSUB	GOTO	IF	INKEY$	INPUT
INPUT#	INT	LOG	LPRINT	MID$	NEXT
OPEN	OR	PRINT	PRINT#	READ	REM
RETURN	RND	SQR	STEP	STOP	STRING$
TAB	THEN	TO	VAL	WIDTH	WRITE#
+	–	/	*	=	>=
<=	^				

The programs have been written as far as possible in an open, readable format, so there are some inefficiencies in their structure. This was unavoidable because I felt that it was more important to write straightforward code. They should be read as integral parts of the text. Their organization follows as closely as possible the accompanying description of the technique and the equations. Memory requirements for the programs and data files are modest in comparison with contemporary commercial software packages:

PROGRAM NAME	K BYTES
GAUSSGEN	1.3
LINCALIB	7.8
SPLINE	11.7
CURVEFIT	10.9
OCTABLE	2.2
OCCURVE	3.7
GMREG	5.0
QCNAME	1.3
QCFILER	1.9
VMASKA	8.3
REPORT	7.6
TOTAL	61.7

Data files require 1.5 K Bytes each.

Overall I have aimed to provide a relevant resource of fully documented computer programs which can be used, as the modules, for an objective quality-control scheme suitable for use throughout most analytical laboratories.

The programs presented in this book are available on floppy disk from the publishers: Ellis Horwood Ltd., Market Cross House, Cooper Street, Chichester, West Sussex, PO19 1EB, U.K. Several disk formats will be available, including IBM–PC and Apple II; please contact the publishers for further details.

1

Calibration graphs

1.1 INTRODUCTION

The analytical method requires that at an early stage in the procedure, the analyst must make some reference to the results of the analysis of a series of standard materials. Quality control should start here, and we therefore have included an extensive discussion on the computerized production of calibration graphs with appropriate statistical tests included to assist with the objective assessment of their quality. If the calibration data fail these tests, it is pointless to proceed with the batch of analyses. Because it is known, and is therefore the 'independent variable', the amount of analyte in the standard is plotted along the abscissa and the instrumental response, e.g. absorbance, counts per minute, electrode potential, is plotted on the ordinate. The shape of the calibration graph depends on the nature of the analytical system: it may be:

1. A straight line with a positive or negative slope.
2. A curve that is convex with respect to the abscissa.
3. A curve that is concave with respect to the abscissa.
4. A curve that is concave with respect to both the ordinate and the abscissa.
5. A curve that is convex with respect to both the ordinate and the abscissa.
6. A sigmoid curve with either a positive or negative slope.

1.2 THE LINEAR CALIBRATION GRAPH

A straight-line calibration graph is the form preferred by most analysts because of its well defined statistical properties. Least-squares linear regression analysis is now a well established technique in analytical laboratories, partly as a result of the ready availability of hand-held calculators with a suitable program in the ROM. Unfortunately this easy access to linear-regression analysis has led to its uncritical use. The program we have devised goes beyond the simple derivation of the slope, intercept and correlation coefficient and provides the user with information on the quality of the fit of the calculated linear regression equation to the original calibration data from which it was derived. The program executes the following sequence:

PARTS A and B

Enter the data into the arrays X(N) and Y(N) where N is the number of X,Y data pairs. X = the concentration in the standards and Y = the instrumental response (lines 330–332). Check the data for input errors and correct if necessary (lines 340–348).

PART C

This gives the user the option of a low resolution plot of the data on an 80 column printer (line 360–362). If this is required then a string array A$(41 rows by 61 columns) is set up and the data points are placed into the appropriate positions in this array (lines 418–434). The graph is printed out by lines 452–456.

PART D

Calculation of the intermediate results required for the determination of the regression equation; *y* regressed on *x*:

SX = sum of the *x* data
SY = sum of the *y* data
XY = sum of the products of $x.y$
XX = sum of the products of $x.x$
YY = sum of the products $y.y$
(lines 478–490).

PART E

Calculation of the slope and intercept with their standard deviations and the correlation coefficient.

XM = SX/N = mean of the *x* data; line 498
YM = SY/N = mean of the *y* data; line 500