

**Guidelines for the Expression of Uncertainties
in Surface Chemical Analysis by Auger Electron
Spectroscopy (AES) and X-ray Photoelectron
Spectroscopy (XPS)**

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ABSTRACT

Guidelines are presented for the statements of uncertainty that accompany analytical results from AES and XPS. Recent recommendations are put into context for these spectroscopies to ensure that results are accompanied by the most relevant uncertainty values.

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0 PREAMBLE

0.1 AUGER ELECTRON SPECTROSCOPY (AES) AND X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) are popularly used techniques for the quantitative chemical analysis of the composition of surfaces at the nanometre scale. AES and XPS were first used qualitatively about 25 years ago; Instrumental and metrological developments since that time have improved successively the repeatability, reproducibility, and finally the overall accuracy of AES and XPS. It is therefore understandable that many industrial laboratories using these techniques are now in a position to start to comply with quality management and accreditation schemes such as BS 5750 (ISO 9000)⁽¹⁾ and NAMAS⁽²⁾.

0.2 INTERNATIONAL RECOMMENDATIONS ON THE STATEMENT OF UNCERTAINTIES

Over the last decade a number of documents have been produced under the auspices of international bodies concerned with standardisation, with the intention of harmonising and rationalising statements of measurement uncertainties for all fields of measurement. The most important of these documents are those of the International Standards Organisation ISO/TAG 4/Working Group 3⁽³⁾, the Western European Calibration Cooperation (WECC) Document 19-1990⁽⁴⁾, and the Comité International des Poids et Mesures⁽⁵⁾ Recommendation 1 (C1-1981).

0.3 SCIENTIFIC AND STATISTICAL BASIS

Over the last five years or so, a number of papers in the surface analysis literature have examined, in detail, the sources of uncertainty in AES and XPS measurements^(6,7), and how these propagate through to an uncertainty in the final quantified chemical composition⁽⁷⁻¹⁰⁾. This provides the scientific and statistical basis for the numerical calculation of uncertainties in AES and XPS.

1 INTRODUCTION

The aim of this document is to provide guidelines on the estimation and statement of uncertainties for AES and XPS laboratories wishing to comply with the various quality management and measurement accreditation schemes^(1,2). These guidelines are consistent with the general principles put forward in the above recommendations by international bodies⁽³⁻⁵⁾, and incorporate conclusions from published research as to which sources of uncertainty are typically significant in AES and XPS^(6,7,9,10).

2 OUTLINE AND DEFINITIONS

The analytical measurement of surface chemical composition involves the quantification of features of one or more AES or XPS spectra, using reference data (such as published atomic sensitivity factors) and prior knowledge about the specimen under analysis. The quantity subject to measurement (the Measurand) may be, for example, the percentage of a particular element present, or the thickness of an oxide layer. As for any measurement technique, for this quantification to be reliable two aspects are of great importance. Firstly, the instrument parameters which enter into the computation must be (a) complete, in the sense that all of the significant influences on the result have been identified, and (b) have traceable calibration for the measurement conditions. Therefore, recognised calibration procedures, which may make use of published reference data, or reference materials, should be used.

Secondly, the model used in interpreting the data should be correct and clearly stated. In practice, the model will not be exact but should be appropriate in the context of the circumstances. We may illustrate what we mean by the simple example of roughness measurements. Numerical values of roughness are often quoted for stylus measuring instruments where it is understood that all roughness features smaller than the size of the stylus will be lost. The result, whilst not absolute, is still true and of both high repeatability and reproducibility and is useful within certain limits which are properly appreciated by those familiar with the technique.

Appendix 1 contains a number of useful definitions of metrological terms which we use in the following sections.

3 MATHEMATICAL DESCRIPTION OF QUANTIFICATION

The quantification of an AES or XPS spectrum typically involves the use of a number of equations and/or algorithms to extract values for a number of measurands. Suppose we consider one of these measurands, y , which may be, for example, the thickness of an oxide layer. This is calculated using a quantification which we shall denote by A , applied to a spectrum of measured intensities $c_1, c_2, \dots, c_N$, and auxiliary reference data $r_1, r_2, \dots, r_M$. Thus we can write

$$y = A(c_1, c_2, \dots, c_N; r_1, r_2, \dots, r_M) \quad (1)$$

The function A need not necessarily be written explicitly as a single expression, and indeed may include steps which can only be expressed as algorithms, and which may have no closed-form functional description.

Any analysis of uncertainty begins with the estimation of uncertainties in the input quantities $c_1, c_2, \dots, c_N, r_1, r_2, \dots, r_M$.

It has been conventional in AES and XPS to categorise sources of uncertainty in quantification into random and systematic components. The traditional treatment of these categories is shown in Fig 1. However, recent international recommendations have deprecated this division⁽³⁻⁵⁾. Instead they recommend that "standard deviations" be estimated for each source of uncertainty, both random and systematic. The term standard deviation has a well defined meaning for random uncertainties, and an analogous quantity can be defined for each systematic uncertainty (obtained by assuming that the systematic error is a random variable equally likely to take on any value between two maximum credible bounds). If this approach were followed naively in AES and XPS analysis, the estimation of uncertainties would follow the route shown schematically in Fig 1(b). This is the correct procedure if the customer for a particular analysis demands a single value uncertainty in a single quoted measure. In practice this is almost never what is really required, and the method of estimation and quotation of uncertainties shown in Fig 1(a) is more appropriate, due to several special features of AES and XPS;

- 1) The uncertainty in the measurand is typically dominated by bias errors particular to a) the instrument, b) the sensitivity factors and c) the analytical model used.
- 2) Full analysis of results is typically performed by the AES/XPS specialist and the customer acting in concert. The quotation of a single "combined" uncertainty is only appropriate when results emerge from the combined "analyst and customer".

It would clearly be wrong for the AES/XPS analyst to combine all uncertainties into a single figure before passing on the results of quantification to the customer. The large bias errors, if "rolled-in" to an overall uncertainty figure may make it impossible for the customer to

draw any useful conclusions from the data. One may hope that in, perhaps, 10 years time these bias errors will be better understood and controlled. Until then, the customer needs some significant understanding of AES/XPS, and especially the sources of bias error, in order to draw useful conclusions from AES/XPS measurements. It is therefore appropriate to preserve the distinction between random and systematic uncertainties in the statement of AES and XPS analytical results.

3.1 SOURCES OF RANDOM UNCERTAINTY

For instruments operating in the direct "electron counting" mode, the uncertainty in each measured count value c_i may often be described by Poisson statistics^(7,11). The standard deviation σ_{c_i} in the value c_i can be estimated from

$$\sigma_{c_i} = c_i^{1/2} \quad (2)$$

It should be noted that some types of instrumental problems⁽¹²⁾ can cause this equation to give an overestimate of true uncertainty (eg due to dead-time effects) while other types of instrumental problem can cause it to underestimate the true uncertainty (eg noise in the detection electronics). The conformance to the Poisson nature of count rate fluctuations should be checked⁽¹²⁾.

In beam-blanking or other analogue modes, the standard deviation uncertainties can be estimated by repeated measurement, and an experimental standard deviation S_{c_i} can be calculated from the spectral values $c_i^{(1)}, c_i^{(2)}, \dots, c_i^{(n)}$

$$S_{c_i} = \left[\sum_{k=1}^n (c_i^{(k)} - \bar{c}_i)^2 / (n-1) \right]^{1/2} \quad (3)$$

$$\text{where } \bar{c}_i = \sum_{k=1}^n c_i^{(k)} / n \quad (4)$$

In this case (and also in checking the Poissonian nature of counting statistics mentioned above) it should be noted that many measurements are needed in order to estimate S_{c_i} properly; typically $n=135$ will be needed to estimate S_{c_i} to $\pm 10\%$ ⁽¹²⁾.

3.2 ERROR PROPAGATION

In order to find the uncertainty in any measure, we must trace the effect of the estimated random and systematic errors in the measured spectrum $c_1, c_2, \dots, c_N$ and auxiliary quantities $r_1, r_2, \dots, r_M$. The most appropriate method is the Gaussian covariance propagation law^(3,13). Weise⁽¹³⁾ provides a number of reasons why the Gaussian procedure is preferable.

For uncorrelated random uncertainties, such as those which arise from the Poisson counting statistics of spectral channels, the overall random uncertainty standard deviation, S_y , in the measurand, y , can be calculated

$$S_y^2 = \sum_{i=1}^N \left(\frac{\partial A}{\partial c_i} \right)^2 S_{c_i}^2 \quad (5)$$

This expression assumes that the fluctuations of measured counts in each channel are uncorrelated, which may not be the case if

- 1) the spectrum has been smoothed prior to quantification,
- 2) the AES/XPS data system, by some algorithm, calculates the "effective" number of counts in some notional channels⁽¹²⁾.

Special care should be taken in the case of correlated uncertainties. These can often arise at an intermediate stage in quantification of a spectrum; an example is in peak fitting, where parameters describing one or more spectral peaks typically have correlated uncertainties. An example in Fig 2 contains computer-simulated data showing that the parameters describing such peaks (full width half maxima, intensity, asymmetry etc) usually have correlated uncertainties, especially when peak overlap is significant. In such cases, if uncertainties in one or more measurements calculated from these parameters are to be quoted in the analytical report, the full covariance matrix form of the Gaussian error propagation procedure should be used^(4,13,14). This is sometimes known as the "Hessian Matrix Method", since the Hessian matrix is the inverse of the covariance matrix. The use of correlation coefficients⁽¹⁴⁾ provides an alternative formalism for taking account of correlated uncertainties. Cumpson and Seah⁽⁷⁾ have enumerated the possible approaches to the treatment of correlated uncertainties of this kind. If appropriate software is not available for the proper treatment of correlated uncertainties via the covariance matrix, then their conservative "projection" method of estimating standard deviation should be used, followed by adding in quadrature according to Eq.(5). This may result in the overestimation of the extent of any confidence interval around a measured value derived from these intermediate "peak-fitting" parameters.

3.3 SYSTEMATIC UNCERTAINTIES

No general rules can be given regarding the estimation of systematic uncertainties; each requires a good understanding of the behaviour of the particular spectrometer in question.

Sometimes systematic uncertainties are known as "influence quantities" to emphasise the fact that they differ from measurands only in that one has less information describing them. Powell and Seah⁽⁶⁾ have surveyed sources of error in AES and XPS and provided two worked examples.

In some works⁽¹⁵⁾ the useful distinction is made between Locally Systematic Errors and Strictly Systematic Errors with their relevant uncertainties. The strictly systematic errors are those usually associated with errors of method or model so that all researchers using a given model or reference data will incur the same systematic error. Estimates of these uncertainties should always be given separately from the other terms. A locally systematic error, sometimes referred to as singly sampled random errors would be concerned with the local experiment. One of the best ways of uncovering the extent of local systematic problems is to take part in proficiency tests or inter-laboratory comparisons.

Often the analyst will only be able to estimate upper and lower credible bounds for a particular source of systematic error. In this case the bounds should be stated explicitly in the reporting of results. Suppose the upper and lower bounds on a quantity r_j (emission angle for example) are r_j^{upper} and r_j^{lower} . Then the value of r_j used in quantification should, if r_j^{upper} or r_j^{lower} are not too different, be given by

$$r_j = \frac{1}{2} (r^{\text{upper}} + r^{\text{lower}}) \quad (6)$$

Even though these bounds represent the extent of a possible systematic error, a quantity u_{r_j} , analogous to a standard deviation, may be calculated

$$u_{r_j} = \frac{1}{2\sqrt{3}} |r^{\text{upper}} - r^{\text{lower}}| \quad (8)$$

This relation gives the correct standard deviation for a random variable with a rectangular distribution defined by the above bounds.

4 STATEMENT OF UNCERTAINTIES

For research purposes it is common to quote uncertainties as the standard uncertainty or 68% confidence limits. Thus, our measure is

$$M \pm S_m \quad (68\% \text{ or higher confidence limits}) \quad (9)$$

For work where the customer will be in a separate field and wishes to know the interval in which the true result is likely to be, a combined expanded uncertainty

$$M \pm kS_m \quad (95\% \text{ or higher confidence limits}) \quad (10)$$

is used where the coverage factor k is most often 2. This gives 95% confidence limits. The factor of 2 is commonly used in chemical analysis in both BSI and ISO standards. It is the value one would expect to provide in production, forensic and other routine analytical situations. In these cases S_m would be the combined uncertainty and kS_m the combined expanded uncertainty, ie all random, locally systematic and strictly systematic uncertainties would be involved in the combined uncertainty as described in the CIPM 1980⁽⁵⁾ procedure where all separate standard deviation or standard deviation estimates are added in quadrature.

For research work, in general, S_m in Eq.(9) will be a standard uncertainty which incorporates random and locally systematic terms alone. Only if the work is researching the method or is generating reference materials or reference data will the strictly systematic terms be considered. In our view, because data are often reinterpreted or further analysed by the customer it is best to quote the random and locally systematic errors (and strictly systematic errors on the occasions when they are considered) separately, in a text form, so that there can be no confusion regarding their origin or confidence limits.

It is probably worth giving some more detailed examples of the way uncertainties may be quoted. Here we shall use, consistently, standard uncertainties. The energy of the aluminium metal 2p peak in XPS may be defined as E_1 with a standard uncertainty of a_1 due to the random effects of the counting statistics and a systematic uncertainty of b_1 due to calibration of the spectrometer energy scale (note that b_1 is not the difference between the indicated energy and that deduced in a proper calibration, it is the uncertainty in applying the correction deduced from that difference). We should then quote the energy as $E_1 \pm (a_1^2 + b_1^2)^{1/2}$. However, if we measure the aluminium oxide peak immediately after that of the metal the shift is $E_2 - E_1 \pm (a_1^2 + a_2^2)^{1/2}$, which is clearly of much better accuracy than the value $E_2 - E_1 \pm (a_1^2 + b_1^2 + a_2^2 + b_2^2)^{1/2}$, deduced if only the global uncertainty is given for each peak position. If the two measurements were widely separated in time, of course, the latter global value would be the figure to use. If, therefore, global values of uncertainty are quoted as required by refs 3 and 5, we should not be able to interpret the data any more fully than the extent provided by the producer of the original data. For legal or conformance work it may be that we do not wish the recipient of the data to attempt further interpretation

and then the global value protects us. However, for research purposes, the global figure is often inappropriate.

We may take a second example in quantification. We may measure the intensities of peaks I_i with random uncertainties a_i and wish to quantify the data using the well known formula⁽¹⁶⁾

$$X_i = \frac{I_i/I_i^\infty}{\sum_j I_j/I_j^\infty} \quad (11)$$

where I_j^∞ are relative sensitivity factors. We may either convert the measured intensities to true intensities, allowing for the spectrometer transmission function, and use standard sensitivity factors or use sensitivity factors I_j^∞ appropriate to our instrument directly. These sensitivity factors have systematic uncertainties b_j and we may then deduce the uncertainty in X_i using Eq.(5), discussed earlier, to give a global uncertainty. If, however, X_i is used in some further relation, such as diffusional or segregation analysis, to deduce activation energies or some similar parameter, the systematic uncertainties in the sensitivity factors may be ignored as, for these calculations, they are self cancelling. To include the global uncertainties would lead to a large overestimation of the uncertainties in these deduced parameters. On the other hand, even if we have quoted the result as $X_i \pm (a_i^2 + b_i^2)^{1/2}$ this will not guarantee the limits of uncertainty as we have ignored the matrix factors in Eq.(11). The errors associated with these are really not yet well defined. However, let us assume we can deal with the problem. In a sense Eq.(11) is still a gross approximation since XPS is used in situations where the surface composition differs from that of the bulk, ie there is a composition-depth profile. In this case we really need angle-resolved or other detailed measurements to define the depth profile with its associated uncertainties. In an ideal world with unlimited time we may make all of these measurements, and more, to analyse the sample fully. However, in practice, the real problem may be solved by the efficient use of a simple analysis as in Eq.(11) without further work. Therefore, it is recommended that the analyst uses whatever calculations his experience or relevant documentary standards indicate are appropriate to the task in hand and quotes separately the standard uncertainties of 1) the randomness of the measurement and 2) the systematic contributions to the expressed result *within the framework of a stated model* which the analyst views to be appropriate.

ACKNOWLEDGEMENTS

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APPENDIX 1

Definitions

A number of relevant terms are defined in the International Vocabulary of Basic and General Terms in Metrology. The following definitions were selected from this document by Powell and Seah⁽⁶⁾ as being most useful in the surface analytical field.

- 1) *Measurand*: A quantity subjected to measurement.
- 2) *Accuracy of measurement*: The closeness of the agreement between the result of a measurement and the (conventional) true value of the measurand.
- 3) *Repeatability of measurements*: The closeness of the agreement between the results of successive measurements of the same measurand carried out subject to all of the following conditions: the same method of measurement, the same observer, the same measuring instrument, the same location, the same conditions of use, repetition over a short period of time. Repeatability may be expressed quantitatively in terms of the dispersion of the results, for example the standard deviation.
- 4) *Reproducibility of measurements*: The closeness of the agreement between the results of measurements of the same measurand, where the individual measurements are carried out changing conditions such as: method of measurement, observer, measuring instrument, location, conditions of use, time. Reproducibility may be expressed quantitatively in terms of the dispersion of the results, for example the standard deviation.
- 5) *(Absolute) error of measurement*: The result of a measurement minus the (conventional) true value of the measurand.
- 6) *Random error*: A component of the error of measurement which, in the course of a number of measurements of the same measurand, varies in an unpredictable way.
- 7) *Systematic error*: A component of the error of measurement which, in the course of a number of measurements of the same measurand, remains constant or varies in a predictable way.
- 8) *Experimental standard deviation, s*: For a series of n measurements of the same measurand, the parameter s characterising the dispersion of the results and given by the formula

$$s = \left[\sum_{i=1}^n (x_i - \bar{x})^2 / (n - 1) \right]^{1/2}.$$

- 9) *Experimental standard deviation of the mean, s_m* : The expression $s/n^{1/2}$, which provides an estimate of the standard deviation of the arithmetic mean $\bar{x}$ with respect to the mean m of the overall population.
- 10) *Bias error (of a measuring instrument)*: The systematic component of the error of a measuring instrument.
- 11) *Traceability*: The property of a result of a measurement whereby it can be related to appropriate standards, through an unbroken chain of comparisons.

- 12) *Uncertainty of measurement*: An estimate characterising the range of values within which the true value of a measurand lies.
- 13) *Limiting errors (confidence limits) of the arithmetic mean of a series of measurements*: The extreme random errors, associated with the arithmetic mean of a series of measurements, which are exceeded with a certain probability. If the errors follow a normal distribution, the limiting errors of $\pm ts$ may be calculated from tables of Student's t values of 1.96 and 2.58 correspond to 95% and 99% probability levels, respectively, and t values of 0.673 and 1.000 correspond to 50% and 68% probability levels, respectively. The 50% limits are known as the probable error.
- 14) *Random uncertainty of a single measurement of a series*: This is simply $\pm ts$.
- 15) *Random uncertainty of the arithmetic mean of a series*: Similarly, this is $\pm ts_m$.
- 16) *Precision of measurement*: The closeness of agreement between randomly selected individual measurements or test results, often given numerically by s .

Some newer items from the ISO/TAG 4/WG 3 Guide to the Expression of Uncertainty in Measurement⁽³⁾ are

- 17) *Standard uncertainty*: Uncertainty of the result of a measurement expressed as a standard deviation.
- 18) *Combined standard uncertainty*: Standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities.
- 19) *Expanded uncertainty*: Quantity defining the interval about the result of a measurement within which the values that could reasonably be attributed to the measurand may be expected to lie with a high level of confidence.

Note: To associate a specific level of confidence with the interval defined by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterised by the measurement result and its combined standard uncertainty. The level of confidence that may be attributed to this interval can be known only to the extent to which such assumptions may be justified.

- 20) *Coverage factor*: Numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty.

Note: A coverage factor, k , is typically in the range 2 to 3. For normal distributions k is given by Student's t values.

CAPTIONS

- Fig 1(a) Estimation of uncertainties in a typical quantification, shown schematically. This corresponds to the "traditional" approach taken for careful analyses performed in AES and XPS. This detailed and categorised statement of uncertainties is particularly valuable when the customer intends to perform some subsequent scientific analysis of the results based on his or her understanding of the AES and XPS techniques.
- Fig 1(b) If required, all sources of uncertainty can be compounded into a single uncertainty in the quoted measure, using the procedure originally set out by CIPM⁽⁵⁾ in 1980. This uncertainty is usually dominated by one or two sources of bias error, which may be the same for many separate laboratories. This global uncertainty is important where the customer may be expected to have no understanding of AES or XPS.
- Fig 2 Results of a Monte Carlo numerical simulation, showing that random errors in fitted parameters become increasingly correlated as peak separation decreases. Each synthesised spectrum consisted of two Gaussian peaks, each of 2000 counts peak height, plus a background of 1000 counts. To each channel, normally distributed noise is added with a standard deviation equal to the root of the number of counts in that channel. Four thousand such spectra were synthesised for each of three possible peak separations and the results of peak fitting, to obtain estimates of each peak height, were plotted as three scatter diagrams; (a) peak separation 4 eV; (b) peak separation 1.2 eV; (c) peak separation 0.4 eV, after Cumpson and Seah⁽⁷⁾.

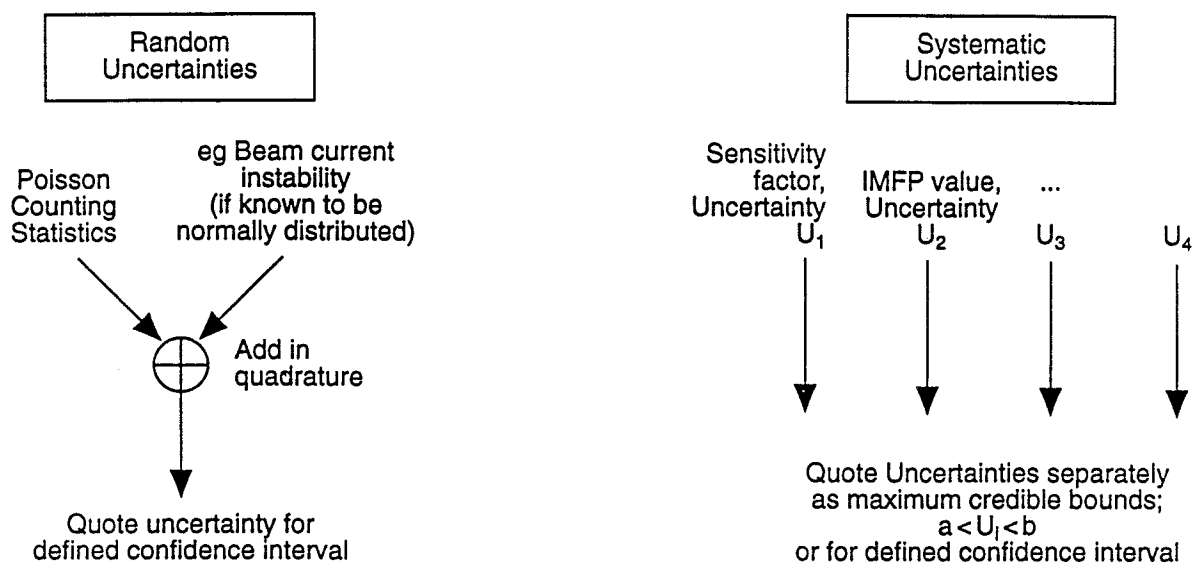


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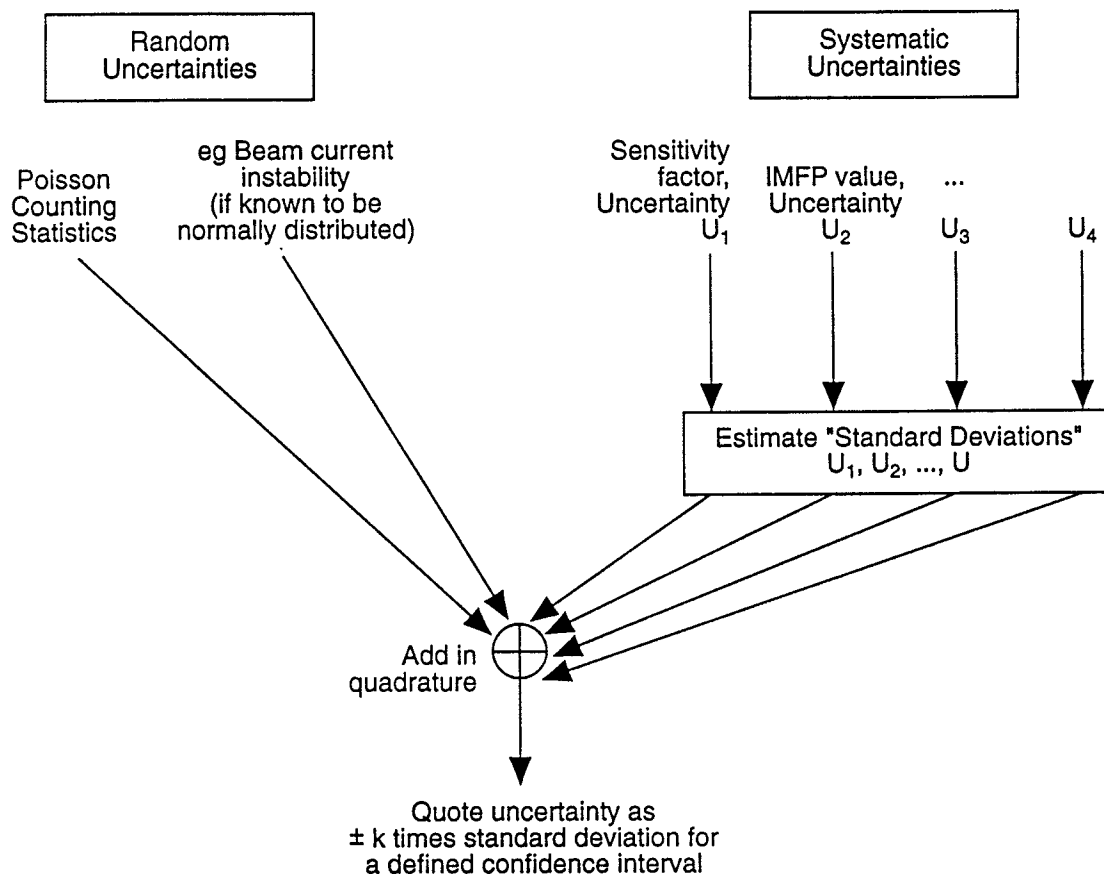


Fig 1(b) If required, all sources of uncertainty can be compounded into a single uncertainty in the quoted measure, using the procedure originally set out by CIPM⁽⁵⁾ in 1980. This uncertainty is usually dominated by one or two sources of bias error, which may be the same for many separate laboratories. This global uncertainty is important where the customer may be expected to have no understanding of AES or XPS.

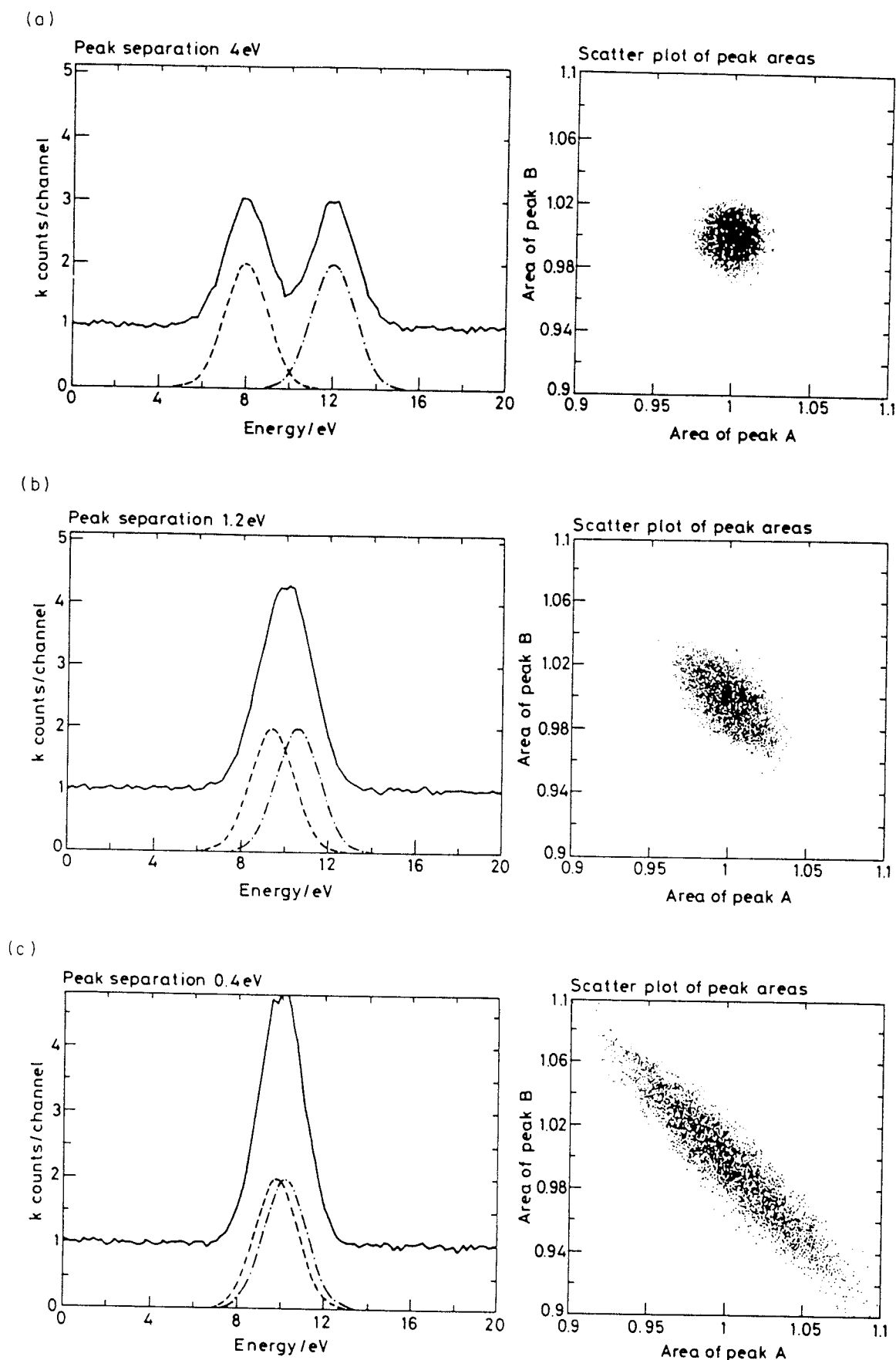


Fig 2

Results of a Monte Carlo numerical simulation, showing that random errors in fitted parameters become increasingly correlated as peak separation decreases. Each synthesised spectrum consisted of two Gaussian peaks, each of 2000 counts peak height, plus a background of 1000 counts. To each channel, normally distributed noise is added with a standard deviation equal to the root of the number of counts in that channel. Four thousand such spectra were synthesised for each of three possible peak separations and the results of peak fitting, to obtain estimates of each peak height, were plotted as three scatter diagrams; (a) peak separation 4 eV; (b) peak separation 1.2 eV; (c) peak separation 0.4 eV, after Cumpson and Seah⁽⁷⁾.