

$^{75}\text{As}^+$ signal due to the changing matrix effects. Upon calibration, both the Be and Si distributions have changed substantially. As expected from the growth conditions, the Be concentration generally increases as the Al concentration decreases and vice versa. In addition, excluding the surface buildup, the Si distribution has generally leveled out at 4×10^{18} atoms/cm³. Without SLIC, this type of analysis could not have been made.

In summary, SLIC is a very precise program for applying calibration lines to the problem of matrix effects in complex samples. Although most of the work to date has been applied to $\text{Al}_x\text{Ga}_{1-x}\text{As}$ matrices, this procedure can be used in related matrices, such as $\text{In}_x\text{Ga}_{1-x}\text{As}$ and $\text{GaAs}_{1-x}\text{Sb}_x$. In addition, work in this laboratory indicates that similar methods can be applied to group III and V compound matrices in which several elements are changing simultaneously.

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Registry No. Al, 7429-90-5; As, 7440-38-2; Ga, 7440-55-3; Si, 7440-21-3; B, 7440-42-8; Be, 7440-41-7.

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Estimation of Detection Limits in X-ray Fluorescence Spectrometry

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The definition of minimum detection limit in instrumental analysis is frequently based on a statistical criterion. Because the magnitude of the detection limit is often derived by extrapolation from much higher concentration, the validity of the value is uncertain. An artificial analytical experiment has been conducted which allows measurement of a low-level signal both with and without contribution from any appreciable background. X-ray measurements at the low count rates expected at concentrations approaching the extrapolated X-ray fluorescence detection limit indicate that the statistical criterion provides a reasonable estimate of the minimum quantity which can be detected.

Many instrumental analytical techniques use a statistical criterion to define the minimum limit of detection, c_L . In recent years there has been general agreement that the determining factor for estimating the limit of detection is the variability of the background, or blank, contribution to the measurable. It has been commonly accepted that c_L is the concentration that produces a signal equal to some constant times the standard deviation of the blank as represented by the equation

$$c_L = ks_{bl}/H$$

where k is the constant (referred to as "k value"), s_{bl} is the standard deviation of the blank, and H is the sensitivity (slope of the calibration curve). The magnitude of the k value has been chosen by various workers to be 2 (for 95% confidence), 3 (for 99% confidence), $2 \times 2^{1/2}$ (for 95% confidence when the signal and blank require two separate measurements and the signal is approximately equal to the blank), and so forth.

The International Union of Pure and Applied Chemistry (IUPAC) recommends that the k value should be 3 (1) and further suggests that, because the values for the blank, and the standard deviation thereof, are estimates based on limited measurements, the $3s_{bl}$ value corresponds to a confidence level of about 90%.

In X-ray fluorescence determinations, minimum detection limits, using the IUPAC criterion, are estimated to be in the range of a few nanograms per square centimeter for thin samples of many elements using commercial instrumentation (2, 3). Laboratory measurements under specialized conditions such as for high energy particle excitation or using synchrotron radiation sources suggest that detection of a few picograms can be achieved (4, 5). There has been a lingering concern in the X-ray analytical community that the estimation of c_L by extrapolation from measurements on standards containing several orders of magnitude higher concentrations may not take account of instrumental variations which are negligible at the higher concentrations. Past attempts have been made to accommodate this uncertainty by suggesting that as much as 14 times the standard deviation of the background be used as the "determination limit" (6) (rather than the IUPAC "detection limit" (1)). The American Chemical Society Guidelines (7) recommend a k value of 10 for the "limit of quantitation".

While in the process of attempting to design a means of producing an accurately characterized sample at a concentration which would approach detection limits estimated for synchrotron radiation excitation, a very simple experiment took shape in our minds which would test the statistics and instrumental uncertainties under conditions corresponding to nanogram quantities. This report describes that experiment and discusses its statistical significance.