DISCUSSION

of the H.C. Smit paper, The Use of Kalman Filtering and Correlation Techniques in Analytical Calibration Procedures.

Diane Lambert

Department of Statistics, Carnegie-Mellon University

I would like to thank Professor Smit for his thoughtful paper on one of the most important steps in the measurement process: the calibration which determines how instrument response is translated into concentration units. As Dr. Smit points out, calibration in analytical chemistry is often difficult because the response of analytical instruments changes with time. The response may vary with ambient temperature, line voltage, and contamination that accrues with use, for example. To compensate for such fluctuations, certain U.S. EPA/CLP protocols for GC/MS instrumentation require that the calibration factor be determined every eight hours. At the beginning of a shift, a standard sample with known concentrations of the target chemicals is analyzed and its response factors for the target chemicals are used to quantitate all other samples analyzed in the same shift. In some cases, a standard "check sample" is analyzed at the end of the shift and its response factors are required to be within some percentage of those observed earlier. This calibration method has two major shortcomings. First, the calibration factor is determined by only one sample, and if there are any anomalies in its response factors, they affect all the samples analyzed in the shift. Even small variability in the response factors of standard samples may introduce unacceptable variability in measured concentrations between shifts. Second, the calibration factor is changed every eight hours regardless of how slowly or rapidly instrument response is changing.

In contrast, Dr. Smit proposes that the calibration factor be updated smoothly, based on the behavior of past samples, and that a new standard sample be analyzed only when the estimated imprecision of a measured concentration becomes intolerably large. There are also other perhaps less evident advantages to Dr. Smit's approach. First, the assumptions about the measurement process that justify the updating scheme are all explicit. Drift, measurement noise and system noise are modelled parametrically, so that the adequacy of models can be checked and the updating scheme can be modified if the models are found lacking. For example, in Professor Smit's application concening the determination of chloride in aqueous samples, a quadratic rather than linear model of drift is fit. Second, estimates of model parameters such as background and average drift are convenient for monitoring instrument performance. Third, the procedure automatically provides information about the uncertainty of measured concentrations. It is as important to report how trustworthy reported concentations are as it is to report the measurements themselves.

Prof. Smit has also considered simultaneous injection and measurement of standard and "unknown" samples. There are, however, some questions about his procedure for conventional sequential analysis of samples that I believe have not yet been resolved. For example, how effective is the procedure if samples are analyzed at a rate of one per hour rather than one per minute? What happens when several or hundreds of chemicals, perhaps all at trace levels, are measured for the same sample? In some examples, accuracy was increased by smoothing Kalman filter estimates and in others it was not. What guidance can be given to a laboratory technician? In short, what are the limits of applicability of this calibration method and when should it be authorized?

Prof. Smit has taken an important step towards improving the chemical measurement process. I look forward to his future work on his procedure.