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## ASSESSING AND CONTROLLING LABORATORY APPROACH FOR SAMPLE CONTAMINATION

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### INTRODUCTION

Contamination is a common source of error in all types of environmental measurements. Most sampling and analytical schemes present numerous opportunities for sample contamination from a variety of sources. This paper addresses the problem of assessing and controlling sample contamination and the resulting measurement error. The first part of the discussion examines the different points in the sample collection and analysis process at which contamination for various measurement applications. The next portion deals with the different possible effects of contamination. The last part of the discussion examines the use of blanks to assess and control contamination. Different types of blanks and their respective uses are described. The applicability of control charts to blank measurements is also discussed.

From an environmental sampling and analytical standpoint, contamination is generally understood to mean something that is inadvertently added to the sample during the sampling and analytical process. Although subsequent measurements may accurately reflect what was in the sample at the time the measurements were made, they do not give an accurate representation of the measured characteristic of the media from which the sample was taken.

To minimize error due to contamination, the potential sources of contamination must be identified and eliminated wherever possible. Once a measurement system is established, appropriate types of blanks should be used to define background levels of contamination for the different parts of the sampling and analytical process. Group of recent Ammonia analysis results for years 2000 to 2002 handled by CLEQM will be used as a typical example of the applied approach.

### SOURCES OF CONTAMINATION

Contamination may be introduced in the field during sample collection, handling storage, or transport to the analytical laboratory. After arrival at the laboratory, additional opportunities for contamination arise during storage, in the preparation and handling process, and in the analytical process itself. Contamination and cross-contamination from sampling equipment is equally a problem in other types of environmental sampling (Ross, 1986).

Sample handling in the field is another potential sources of sample contamination. Acids and other chemical preservatives that may become contamination after a period of use in the field offer another route of sample contamination during field handling (USEPA, 1999). Sample containers represent another major source of sample contamination. Plastic sample containers, for example, are widely recognized as a potential source of sample contamination in trace metal analyses (Moody and Lindstorm, 1987). Glassware and reagents are common sources of laboratory contamination in all types of analyses. Carry-over and memory effects from consecutive analyses of high- and low-level samples are also common to many types of instrumental methods, including gas chromatography, liquid chromatography, and many spectroscopic methods (Bagchi, 1986). Common sources of sample contamination are summarized in Table (1).

Table 1. Potential Sources of Sample Contamination (Fetter, 1983)

| Critical Steps in the Sampling and Analytical Process | Contamination Sources   |
|---|---|
| Sample Collection                                     | Equipment and apparatus<br>Handling<br>Preservatives<br>Ambient contamination   |
| Sample transport and storage                          | Sample containers<br>Sample containers<br>Cross- contamination from other samples or reagents   |
| Sample preparation                                    | Sample handling<br>Glassware<br>Reagents<br>Ambient contamination   |
| Sample analysis                                       | Sample handling<br>Syringes used for sample injections<br>Carry-over and memory effects<br>Glassware, equipment, and apparatus Reagents (e.g., carrier gases and eluents) |

## EFFECTS OF CONTAMINATION

Chemical or physical properties of samples that cause errors in the measurement process are commonly known as interference. Generally, two types of interferences are recognized: additive interference and multiplicative interferences (Shacklette and Borngen, 1984). Additive interferences are caused by sample constituents, generate a signal, that adds to the analyte signal. Because they cause a change in the intercept but not the slope of the calibration curve, additive interferences have the most pronounced effect at low analyte contaminations. Multiplicative interferences, on the other hand, are caused by sample constituents that either increase or decrease the analyte signal by some factor without generating a signal of their own. Multiplicative interferences change the slope of the calibration curve not but the intercept.

Multiplicative interferences are a common source of analytical error in many spectroscopic techniques, although matrix effects are a more common source of such error than contamination. Contaminants may, however, cause multiplicative interferences through adsorptive losses of the analyte of interest. These contaminants give erroneously low results. Adsorption acts as a multiplicative interference when a constant fraction of the analyte is adsorbed, regardless of analyte contamination (i.e., when relative bias is constant). When the amount of analyte is large compared to the available sites for adsorption to occur, the amount of analyte lost to adsorption tends to be constant, and relative bias decreases with increasing contamination. In such cases, adsorption causes a negative interference, opposite in effect to an additive interference.

Regardless of the source of sources of sample contamination, the net effect is added inaccuracy in the measurement process. Like other types of measurement error, error due to contamination may be sporadic and represent special causes, or systematic and affect all measurements. Cross-contamination, such as that which often occurs during analysis when carry-over from high-level samples contaminates subsequent low-level samples, is a common source of sporadic contamination. Similarly, careless sample handling and dirty sampling equipment are often sources of sporadic contamination. Sporadic contamination, most often, affects the measurement process by introducing false positive results. A false positive is the error of concluding that an analyte is present in the media sampled when it is not. In the case of sporadic contamination where the contaminant acts as a negative interference, as in dilution or adsorption, false negatives may result a false negative is the error of concluding that an analyte is not present when it is.

Contamination is a source of systematic error when the level of contamination is stable for all samples. Strictly speaking, however, stable, systematic error due to sample contamination is rare. Almost always, some element of sporadic error is associated with any source of contamination. In some cases through, the effect of this sporadic error component is small in comparison to the systematic error, or bias component. Thus, some types of contamination behave in a fashion that is

primarily systematic. Systematic contamination increases the “background contamination” of the analyte of interest and thus affects the lower limit of the measurement process. Contaminated reagents are a common source of systematic contamination in many types of environmental measurements. Contaminated sample containers are another source of contamination that is often primarily systematic.

## USE BLANKS TO ASSESS AND CONTROL CONTAMINATION

The most commonly used analytical tools for assessing and controlling sample contamination are blanks. By conventional nomenclature, blanks are samples that do not intentionally contain the analyte of interest but in other respects have, as far as possible, the same composition as the actual samples. Additional descriptors, such as internal, reagent, field, solvent, and others, are used to indicate which of the various stages of the sampling and analytical process the blanks are considered to represent. Because blanks, by definition, do not intentionally contain the analyte of interest, their utility in assessing and controlling sample contamination is limited to contaminants causing additive interferences. In this regard, results for blanks are taken as a direct measure of the non-analyte, or contaminant, signal for the corresponding samples.

### Types of Blanks

Blanks play various roles in environmental measurements, depending on the analytical technique used and the goal of the blank measurements. Table (2) summarizes the types of blanks typically used in environmental measurements. The simplest blank, often called a system blank or instrument blank, is really not a blank at all the sense of simulating a sample. Rather, a system blank is a measure of the instrument background, or baseline, response in the absence of a sample. System blanks are often used in gas and liquid chromatographic methods to identify memory effects, or carry-over from high-concentration samples, or as a preliminary check for system concentration.

Table (2): Summary of Blank Types (Shacklette and Borngen, 1984)

| Common Name          | Other Names       | Uses  | Description  |
|----------------------|-------------------|---|--|
| Laboratory blanks    |                   |   |  |
| System blank         | Instrument blank  | To establish baseline response of an analytical system in the absence of a sample   | Not a simulated sample but a measure of instrument or system background response                                       |
| Solvent blank        | Calibration blank | To detect and quantitate solvent impurities; the calibration standard corresponds to zero analyte concentration   | Consists only of the solvent used to dilute the sample   |
| Reagent blank        | Method blank      | To detect and quantitate contamination introduced during sample preparation and analysis  | Contains all reagents used in sample preparation and analysis and is carried through the complete analytical procedure |
| Field blanks         |                   |   |  |
| Matched-matrix blank |                   | To detect and quantitate contamination introduced during sample collection, handling, storage, transport, preparation, and analysis                               | Made to simulate the sample matrix and carried through the entire sample collection, handling, and analysis process    |
| Sampling media blank | Trip blank        | To detect contamination associated with sampling media such as filters, traps, and sample bottles   | Consists of the sampling media used for sample collection  |
| Equipment blank      |                   | To determine types of contaminants that may have been introduced through contact with sampling equipment; also to verify the effectiveness of cleaning procedures |  |

## Use of Blank Results

When properly used, blanks can be extremely effective tools in assessing and controlling sample contamination and in adjusting measurement results to compensate for the effects of contamination. Used improperly, blank results can increase the variability of analytical data or be very misleading. An important part of using blanks effectively is understanding and recognizing their limitations. As mentioned previously, blanks are ineffective in identifying interferences such as dilution or adsorption. Similarly, blanks cannot be used to spot non-contaminant error sources such as analyte losses due to volatilization or decomposition. Beyond these inherent limitations, the utility of blanks is determined largely by the manner in which they are used and the manner in which the results are interpreted. Blanks serve both control and assessment functions in environmental measurements. In their control function, blanks are used to initiate corrective action when blank values above prestablished levels indicate the presence of contamination. Blanks are most often used in this control mode in laboratory operations where feedback is more nearly real-time. At the first sign of unusual contamination, analyses may be stopped until the source is identified and the contamination eliminated. If possible, affected samples may then be reanalyzed. When field blanks indicate possible contamination, resampling is usually more difficult and often impossible. Therefore, field blank data are generally used primarily for assessment rather than control. If field blank data are used for control, this control is generally accomplished only over relatively long periods of time. In their assessment role, both field and laboratory blank data may be used to define qualitative and quantitative limitations of the associated measurement data. Where appropriate, these blank data may also be used as a basis for adjustments, however, should be made with caution, and the average of multiple blank measurements should be used for a stable, "in control" measurement system.

## Control Charts for Blanks

Whether blank data are used primarily for ongoing control or for retrospective assessment, Shewhart control charts (Shewhart, 1984) provide the most effective mechanism for interpreting blank results. In the control mode, control charts can be used to detect changes in the average background contamination of a stable system. This detection is done by providing definitive limits, based on past performance, that signal when the level of contamination is greater than that which is attributable to chance causes. This signal allows corrective action to be initiated to identify and correct new or additional sources of contamination as they appear, before large numbers of samples are affected. In the assessment mode, control charts allow out-of-control periods to be easily identified so that corresponding sample data may be flagged or interpreted separately from the other data (Grant and Leavenworth, 1980). By identifying out-of-control periods, control charts also allow more reliable estimates to be made of the average background contamination level under normal in-control periods.

## Control Charts for Individual Measurements

The problem of blanks not usually being run in replicate can be overcome by using a control chart for individual measurements. This special type of control chart is useful when no rational sub-grouping scheme arises, when performance measures can only be obtained infrequently, or when the variation at any one time (within a subgroup) is insignificant relative to variation over time (between subgroups).

Although they share the same statistical basis, control charts for individuals (X charts) are different from control charts for means (X charts) and ranges (R charts) in the way the range is calculated and in the sub-grouping scheme. For these reasons, individual control charts are interpreted somewhat differently than usual. In X charts, the chart reflects variability between subgroups (i.e., between means); in R charts, the chart is used to monitor variability within subgroups. In control charts for individuals, however, the range within a subgroup cannot be calculated because the subgroup size is one. Also, because individual measurements are plotted, a single chart combines all sources of variation.

The first step in preparation of an X chart for blanks is to tabulate historical data for blank measurements. This tabulation will consist of at least 20 individual results for the particular type of blank to be charted. After arranging the K results in chronological order, K-1 moving ranges are

calculated, where the first moving range is the range between the second and third values, etc. next, the average of the values, etc. next, the average of the X measurements (X avg). Before calculating the control limits for the individual values, the moving ranges are screened by first calculating the upper control limit for the moving ranges as 3.27MR [The value 3.27 is the D4 value for calculating control limits for ranges having n=2, where n is the number of measurements in each subgroup] . Any moving ranges larger than the calculated control limits are removed, and then the average moving range is recalculated. Finally, the upper and lower control limits (UCL and LCL, respectively) for the individual values are calculated as

$$\text{UCL} = \bar{X} + 2.66 \text{ MR} \quad (1)$$

$$\text{LCL} = \bar{X} - 2.66 \text{ MR} \quad (2)$$

Although not tabulated in many tables of control chart factors, the value 2.66 used to calculate the control limits is the  $A_2$  factor of calculating control limits for  $\bar{X}$ , where  $n=1$ . Unless the average blank value is substantially greater than zero, the LCL may be negative and thus will not be meaningful. Only the UCL can be used in these cases.

In traditional  $\bar{X}$  charts, the underlying assumption is that variability within a subgroup is representative of the system variability. Control limits for  $\bar{X}$  are, thus, derived by using the within-subgroup range to estimate the standard deviation from which the control limits are calculated. In individual control charts, the moving range between subgroups (i.e., between the individual points) is used to estimate the standard deviation. Because pairs of consecutive measurements are more likely to be affected by similar special causes than are results from different points in time, screening the moving ranges prior to calculating the control limits minimize the contribution of these special causes. This screening prevents the control limits from being inflated by these special causes, as would be the case if the standard deviation was calculated by using all the original data points.

In using this approach, the problem still arises of dealing with zero and not detected values in the blank data from which the control limits are to be calculated. In this case, the average moving range must be estimated by using alternate data. Results for low-concentration standard solutions provide the best substitute. Obviously, if the blanks of interest are, for example, matched-matrix field blanks, standards should be prepared in a similar manner by spiking the appropriate matrix with the analyte of interest. In either case, the concentration of the standard should be in the same range as the estimated detection limit (i.e., between 1 and 5 times the estimated detection limit). At this level, imprecision should be of approximately the same magnitude as that for blanks. The actual control limits are calculated by using the average moving range for the standards and the mean blank value for similar blanks.

One limitation that should be considered in using an  $\bar{X}$  chart is the increased sensitivity of the limits to the distribution of the measurements.  $\bar{X}$  charts are less sensitive than  $X$  charts to the distribution of individual measurements because mean values are used. Means tend to be normally distributed. Because contamination tends to induce positive errors in blank measurements, the resulting distribution is likely to be skewed toward positive values. If inspection of the results indicates positively skewed values, the measurement data should be transformed prior to developing the control chart, and the transformed data should be charted. A logarithmic transformation is generally most appropriate for environmental data.

## ASSESSMENT OF SAMPLE CONTAMINATION

### Example of an $\bar{X}$ Chart for Blanks

As an example of the development and application of an  $\bar{X}$  chart for blanks, consider the Ammonia data for years 2000 to 2002 analyzed by CLEQM. Assume that the results for blanks 1-24 represent historical data used to develop the example control chart, and the results for blanks 21-65 represent subsequent blank measurements. The completed control chart is shown in Figure (1).

The first step in developing the example control chart was to examine the distribution of the historical data. The raw results are significantly skewed as is often the case for blank data. Therefore, before proceeding further, the raw data were transformed by taking the natural logarithm of each

value. This produced the transformed results A frequency histogram of the transformed data that shows significant improvement in the skewness of the distribution.

The next step in developing the example control chart was to calculate 23 moving ranges for the 24 chronologically ordered transformed results. The UCL for the moving range, 5.24, was obtained by multiplying the average moving range, 1.24 by 4.22. This moving range control limit was then used to screen the moving ranges prior to calculating the control limits for the blank measurements. Screening the moving ranges and removing any values exceeding the control limit prevent the control limits for the blank measurements from being inflated by values representing special causes. The 7<sup>th</sup> moving range (blank number 8), 4.80, exceeds the moving range control limit. Therefore, this value was removed, and the average moving range was recalculated to yield a value of 1.21. Finally, upper and lower control limits for the blank measurements were calculated as the average of the transformed results (-4.03) plus and minus 2.46 times the average of the screened moving ranges (1.21).

The completed control chart for this example, shown in Figure (1), illustrates how control charts for blanks are effective tools both for ongoing control and for retrospective assessment of blank results. In the blank indicate unusual contamination from an assignable cause and should initiate corrective action to identify and eliminate the source of additional contamination. In the case of field blanks, analyzing the samples and plotting the results may not be possible until after all of the samples are collected. In such cases, control charts are still useful in assessing the blank data by indicating both sporadic and systematic contamination problems and allowing the corresponding measurement data to be interpreted accordingly. The example control chart in Figure (1), for instance, shows shift in background contamination during the course of the hypothetical sampling and analytical effort. Such a shift might be the result of a change in sampling or analytical procedures, a change in personnel, a new lot of sample bottles, or any one of a number of other possibilities. Identification of these types of changes in background contamination allows field sample data to be ground and interpreted separately even if it is already too late eliminate the new source of contamination.

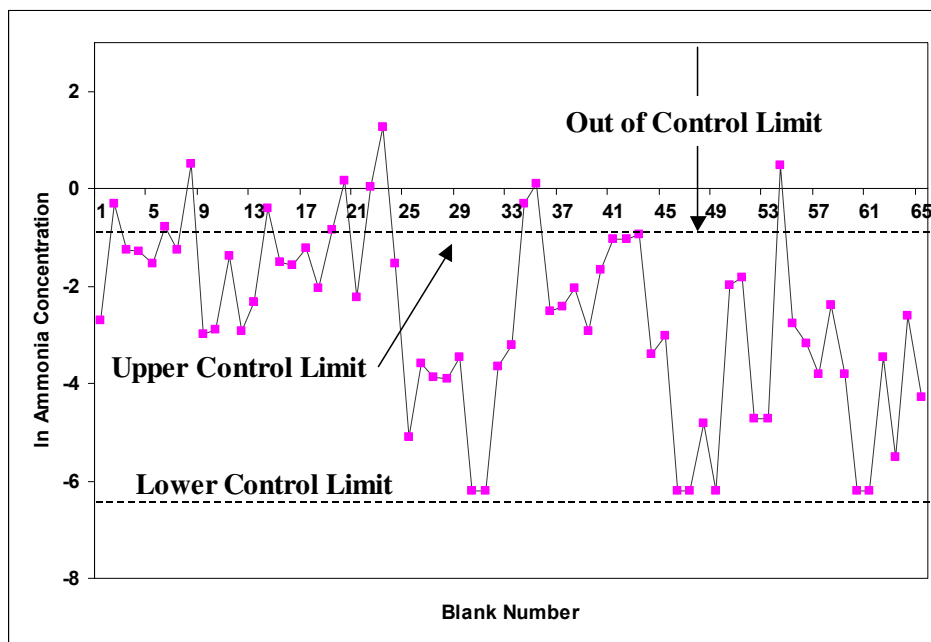


Fig. 1. X chart for Ammonia blank measurements

### Assessing the Effectiveness of control Charts for Blanks

The key role of control charts in controlling contamination is in detecting out-of-control points in an otherwise stable measurement process. Although results inside control limits do not indicate the absence of contamination, they are an indication that the effect of contamination is stable. In such a

case, systematic adjustment of the measurement data using the average blank value to correct for the background contamination may be appropriate. Blank results that fall outside control limits provide a signal that some new source of contamination has entered the measurement system. Just as establishing the absence of any given analyte in a sample is analytically impossible, establishing the absence of contamination in a measurement process by analyses of blanks is also impossible. The best that can be achieved is to reduce the risk of not detecting contamination to an acceptable level.

In assessing this level of risk in using blanks to detect changes in contamination, the frequency of the blank measurements, the magnitude of change in the level of contamination that one desires to detect, and the amount of variability in the measurement system must be considered. Using three-sigma limits on the average of  $n$  measurements, the probability,  $P$ , of not detecting a bias (Burr, 1976)

$$P = \Phi \left\{ \left[ \frac{(n)^{\frac{1}{2}} b}{\sigma} \right] \right\} - \Phi \left\{ -3 - \left[ \frac{(n)^{\frac{1}{2}} b}{\sigma} \right] \right\}$$

of size  $b$  when the measurements are normally distributed and have a standard deviation of  $\sigma$  is

Where  $\Phi$  is the cumulative distribution function of the standard normal distribution. The probability of detecting a bias of size  $b$  in  $m$  independent tests (each based on the average of  $n$  measurements), or  $P_D$ , is (Provost and Elder, 1985)

$$P_D = 1 - P^m \quad (3)$$

Where  $m$  denotes any power of  $P$ .

Consider, for example, a case in which an X chart is used monitor blank results for a particular analyte. In this case, historical data indicate that the average blank concentration of this analyte is 3 ppb, and the standard deviation is 4 ppb. What is the probability of detecting contamination greater than 10 ppb in a single blank? Because 10 ppb represents an increase of 7 ppb above background,  $b = 7$ . The subgroup size for X charts is one, so  $n = 1$ . In this case,  $m = 1$  also because a single point on the control chart. Therefore,

$$\begin{aligned} &= \Phi(1.25) - \Phi(-4.75) \\ &= 0.894 - 0.000 \\ &= 0.894 \end{aligned}$$

and

$$P = \Phi \left\{ 3 - \left[ \frac{(1)^{\frac{1}{2}}(7)}{4} \right] \right\} - \Phi \left\{ -3 - \left[ \frac{(1)^{\frac{1}{2}}(7)}{4} \right] \right\}$$

$$\begin{aligned} P_D &= 1 - (0.894) \\ &= 0.106 \end{aligned}$$

Thus, the probability of detecting an additional 7 ppb of contamination is only 11% for a single blank analysis. If the additional contamination is from a constant source, the probability of detection improves somewhat with repeated measurements. However, because the standard deviation is relatively large compared to the added contamination, 24 measurements are required to attain a greater than 90% probability of detection. On the other hand, a shift of 20 ppb for the same measurement system would have a greater than 97% probability of being detected in a single measurement. Figure (2) illustrates the relationship by showing probabilities of detecting unusual contamination in a single blank analysis for measurement systems having standard deviations of 3, 5 and 7 ppb. Contamination levels as high as 40 ppb are illustrated.



Control charts are most effective tool for detecting contamination when measurement variability is small relative to the level of contamination to be detected. Many measurements may be required to detect small shifts in background contamination. Also, in order for such shifts to be reliably detected even through repeated measurements, the additional contamination must be persistent. An assumption in equations 3 and 4 is that the problem persists at the same level until corrected. Although reasonable for many sources of contamination, this model is not applicable in all cases. If contamination occurs sporadically at low levels, then detecting the changes in contamination levels is much more difficult. In such cases, the only reasonable approach is to work on identifying eliminating the source or sources of contamination.

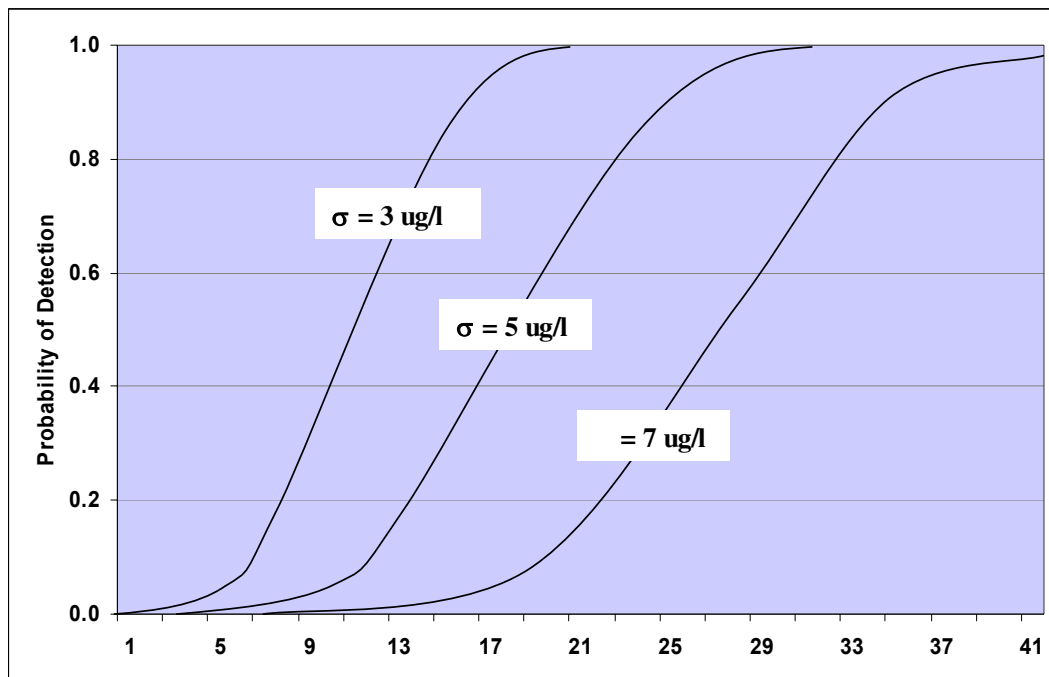


Fig. 2. Relationship between measurement variability and probability of detecting unusual contamination in a single blank measurement

## CONCLUSIONS

Environmental sampling and analytical efforts numerous opportunities for sample contamination from a wide variety of different sources. Regardless of the source of contamination, the accuracy of the measurement process is affected. Because environmental measurements often address very low concentrations of analytes, contamination is an especially important source of potential error. To minimize error due to contamination, the potential sources of contamination must be identified and eliminated wherever possible.

Once a measurement system is established, appropriate types of blanks should be used to define background levels of contamination for the different parts of the sampling and analytical process. Blanks should also be used on an ongoing basis to assess and control contamination. In the assessment mode, the information provided by blanks may be qualitative or quantitative; blanks may be used as qualitative indicators of possible sample contamination or to derive quantitative estimates of background contamination levels. In the control mode, blanks are used to initiate corrective action when results above prestablished levels indicate unusual contamination.

Whether used primarily for assessment or for control, control charts should be used to maximize the effectiveness of blank measurements. Control charts for individual measurements, or X charts, are usually more appropriate for blanks than the more common X and R charts. Other types of control charts may be applicable or preferable under certain circumstances. Regardless of the type of control chart used, the risk of not detecting new sources of contamination in a measurement system depends upon the number of blank measurements, the magnitude of the effect of the new contamination, and the variability of the measurement system. This risk should be a primary consideration in developing the overall quality control strategy. By recognizing potential sources of contamination and using blanks to detect changes in background levels, reducing or correcting for contamination is generally possible, and the associated measurement biases can thus be reduced to acceptable levels.

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