CHAPTER 9

Laboratory Contamination

Laboratory contamination is defined as the inadvertent addition of target analytes to samples during the sample collection, transportation and analysis process. Just like the adage that the best place to catch a disease is in the hospital, the best place to find an environmental pollutant is in an analytical laboratory. Contamination manifests itself in the detected presence of target analytes in the sample that are in greater amounts than they are in the native source of the sample. In 1994 EPA announced that all the ambient monitoring data that had been collected for over 30 years in more or less pristine sites in an ongoing effort to define the natural background levels of heavy metals was unreliable due to contamination in sample collection and analysis. Oceanographers have discovered in the last 10 years that historically determined ambient ocean metals levels are heavily biased due to the presence of the metal hull of the ship used for the research. Although a majority of the attention has been directed toward metals, contamination issues are not limited to the metals in inorganic analysis.

Reporting elevated amounts of target analyte in a particular sample above that present in the sample source is the most visible manifestation of laboratory contamination, but there are other effects that in many ways are more serious. Chief among these is the question of advertised detection limits of the laboratory. Based on many years as a quality assurance manager in an environmental laboratory I can state without any reservation that unless a laboratory has a specially constructed clean room and it is maintained and monitored under the strictest protocols, detection limits less than 20 ug/L for copper, aluminum, zinc, iron, and nickel, and less than 50 ug/L for sodium, calcium, magnesium, and potassium are unachievable. The problem is not with the instruments, rather its is due solely to contamination. An example of contamination and one effect on realistic detection levels is illustrated in the calibration plot presented in Figure 6-11.

All laboratories have contamination problems, and these problems are unavoidable and largely insurmountable without significant investment in construction and maintenance of clean room facilities. Clean rooms are designed[1] to minimize laboratory contamination in metals analysis.

The single most significant item that contributes to inorganic contamination is dust. Almost all persons at one time in their life or another have had occasion to sit watching dust motes floating in the air through a sunbeam while their thoughts wander off into eternity. When I was young I imagined that I was seeing atoms and molecules. What I was actually seeing was only the very large dust particles, not even remotely close in size to the atomic or molecular scale. Many particles, such as those that compose smokes, are much too small to be seen as individual particles even in a sunbeam.

Dusts are composed of both inorganic and organic materials. Some dust particles are formed from the slow weathering of solid objects while others are created from active biological or chemical processes upon materials. One chemical process that contributes substantial quantities of dust to the air is combustion. Air-suspended particles range in water content from very dry particles to microdroplets of water that form around a solid nucleus. Fogs and clouds are the most commonly encountered form

[1]EPA Office of Water, 1995. *Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities*. USEPA 821-B-95-001.

of the microdroplet particle. Particles with a high water content tend to stick to solid objects easier than dry particles. Dust particles are almost always heavier than air, but it is actually the ratio of weight to volume (density) and physical size that determines transport ability through the air. Dense dust particles will quickly settle out from the air and coat everything. Less dense particles can be suspended in the air for very long periods of time.

The major intent of the clean room is to minimize metal-containing dust. This is primarily achieved by filtration of the air entering the room through high efficiency particle attenuation (HEPA) filters which remove all categories of particulates. The clean room is operated under positive pressure so that the flow of air is always out of the room, and the only air entering the room must pass through the HEPA filters.

A second, although also important concern, is to minimize the creation of metal-containing particulates within the clean room. This is achieved by elimination of as many metallic objects within the room as possible. Trace metals laboratories utilize strong, corrosive acids for sample preparation, and invariably these acids produce acid vapors that hasten the corrosion of any metal items. Thus structural and accessory items in the room such as the walls, floor, ceiling, ducting, benches, stools, hoods, sinks, doors, miscellaneous laboratory equipment, reagent containers, *etc.*, are made of plastics. This includes faucets and plumbing. Items that must contain metals such as the electrical and lighting system and laboratory devices such as balances and hot plates are isolated from the room as much as possible or coated/encased with plastics (epoxy paint or silicone glue) to minimize exposed metal surfaces and components.

The clothing that technicians wear can serve as a transport mechanism for metal-containing particulates from one part of the laboratory to another. Thus provisions must be made to eliminate this source of contamination by requiring clothing to be changed as technicians enter and exit the clean room. In the most successful and elaborate designs, a clean room actually consists of a series of dead-space connected rooms that progress in cleanliness from the regular parts of the laboratory to the clean areas involved with sample preparation, sample container preparation, and analysis.

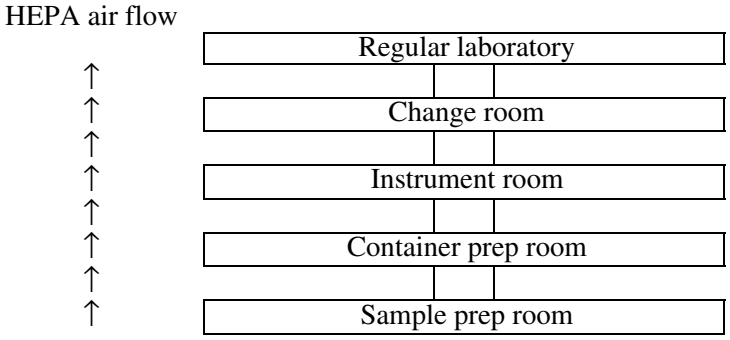

Figure 9-1. Schematic of trace metals clean room facility.

The simple possession of a clean room facility does not by itself resolve the contamination issue. Operational procedures must be used that actively minimize the levels of contamination within the area. Access to the clean room is limited to those persons who are well versed and constantly aware of clean techniques.

Reagents that are used in sample preparation and analysis must be the highest quality available. Acids must be free from trace metal contamination. The most suitable acids are prepared by sub-boiling distillation. Acids purified by this technique are commercially available; however, the apparatus to perform this purification is reasonably priced and over the long-run will pay for itself.

A significant area that presents a potential for contamination is the presence and use of quality control standards for matrix and blank spiking in the sample preparation room. Extreme care must be exercised in keeping the standards and pipettes used for spiking separated from the analytical samples. It only takes one small drop of a spike solution to contaminate a sample.

Metals laboratories have developed a phobia about the use of glassware based on the belief that glass interacts with the metals in solution. The interaction is believed to be an ion exchange phenomenon with heavy metals in solution being exchanged for the light metals in the glassware. Further this phobia has led to the belief that plastics, particularly fluorocarbon plastics, are the best overall replacement for all uses of glass in the metals lab.

Without any qualification, there is no plastic volume measurement system, such as a micropipettor with disposable plastic tips or a plastic volumetric flask, that is as reliable as the Class A volumetric glassware. Micropipettors can be adjusted to deliver volumes of liquids with the accuracy of Class A glassware; however, they are high-maintenance devices, requiring complete disassembly and lubrication followed by recalibration about every three weeks. They should be checked for accuracy at least weekly to assure that the correct volume is being delivered. The first symptom that a micropipettor needs maintenance is loss of precision in volume delivery due to leakage around the plunger. Further, each new lot number of disposable tips must be checked to insure that they are free from contamination.

Yes, it is true that elemental standard solutions should be stored in either fluorocarbon or high density polyethylene bottles rather than glass because ion exchange can occur during the sometimes lengthy storage times. Plastic containers, except for the fluorocarbon polymers, are also considerably cheaper than glass, and can be treated as disposable. However storage instability is no reason to avoid using acid-washed Class A volumetric glassware for accurate preparation of the solutions. A plastic volumetric flask is only calibrated to Class B tolerances and, further, is much more susceptible to thermal contraction and expansion than is a glass flask. The contact time with the glassware is generally less than 2 or 3 minutes, which is insufficient time to alter the composition of the solution. A glass volumetric flask is not a storage container. After accurate volume adjustment is made, the solution is immediately transferred to a plastic storage bottle.

Plastic bottles are not suitable for storage of mercury standards, samples, or solutions as has been demonstrated many times. Mercury is easily reduced to the elemental state even in the presence of nitric acid. In the zero-valent state mercury is able to dissolve into the walls of the plastic containers. Even more significant, mercury in cationic form is not inert to organics. There are numerous examples where mercury adds to unsaturated organic molecules in the well-characterized oxymercuration reaction to form a covalent carbon-mercury bond.

$$Hg(NO_3)_2 + H_2O + R_2C = CR_2 \text{ --> } O_3NHg\text{-}C(R_2)\text{-}C(R_2)OH + HNO_3$$

Mercuric acetate is normally the preferred reagent for this reaction when it is performed in organic synthesis; however, mercuric nitrate is known to be even more active than the acetate. Most plastics, such as the polyfluorocarbons and the polyethylenes, are formed from monomers with a double bond, tetrafluoroethylene and ethylene, and there are always residual double bonds in the plastic, enough to completely deplete a low concentration standard or sample of mercury. Mercury standards, samples, and solutions must be stored and manipulated in glass.

Numerous laboratories have resorted to using digestion containers made of inert plastics, such as the polyfluorocarbons, in an effort to avoid contamination problems. While not initially contaminated, polyfluorocarbon containers can become metal-

contaminated with use[2]. A cleaning technique that includes a weekly soaking with a strong chelating agent such as EDTA can satisfactorily correct this problem.

Metals are not the only inorganic analytes that are subject to laboratory contamination. The common anions nitrate, phosphate, sulfate, and chloride are ubiquitous in the environment and in the laboratory. Ammonia, being a gas at room temperature, tends to permeate the air of the laboratory whenever a bottle of reagent ammonia is opened, and can contaminate both standards and samples. Laboratory practices that help to lessen the contamination problem are the use of dedicated glassware and reagents for each procedure and performing the individual analyses in isolated sections of the laboratory rather than out in large common work spaces. Although the following suggestion may seem to be anathema to laboratory managers who tend to rigorously segregate organic from inorganic analysis, in fact, a judicious mixing of organic and inorganic work areas can help reduce laboratory contamination problems. Performing TKN and ammonia analysis in the volatile organic analysis area helps prevent the airborne contamination problems that are common to both procedures. Phosphate analysis performed in the organic extractions lab tends to make sense as the two functions have no reagents in common, while anion instrumental analysis can be performed in the organic instruments area. This mixing of lab procedures also helps in maintaining dedicated glassware sets. For example, few extractions technicians would think of using the equipment that a phosphate analysis might require.

A. Contamination from Sampling

A significant potential source of contamination is the sampling procedure. Prevention of contamination begins with consideration of the containers used for the sampling. Regardless of any contamination-minimizing procedures used during the analysis, a contaminated sample container will bias the results. Containers should be washed with a suitable (analyte-free) detergent and rinsed sequentially with analyte-free mineral acid(s), and reagent water.

Containers purchased as pre-cleaned must be checked by lot to insure that they are clean. This is performed by adding analyte-free reagent water to a randomly selected container from the lot, adding the preservative that will be used in the sampling, then testing the contents of the container as a sample. This serves as a check on the both the cleanliness of the container lot and the suitability of the preservative reagent. Each container lot must be checked. Suppliers of containers employ people who make mistakes just like everyone else. One lot of plastic bottles intended for nitrate sampling was found that had been rinsed by the commercial supplier with nitric acid. It was not intentional and the supplier gladly replaced the bottles, but mistakes do occasionally happen, and the laboratory has to be on guard to catch them.

An additional check that can be performed is addition of a solution containing a known amount of the target analyte to a randomly selected container along with the preservative, then holding the spiked container for the maximum holding time under the normally prescribed storage conditions prior to analysis. The recovery of the target analyte checks for the holding time and storage condition suitability of the container and preservative. It is a given that this procedure is going to involve some time, and that normally a purchased lot of containers can not be held for 14 days to 6 months

[2] Smith, R-K., and F.B. Secord, 1995. "Removal of zinc contamination from Teflon® PFA microwave digestion vessels." *Proceedings of the Eleventh Annual Waste Testing and Quality Assurance Symposium*, EPA and ACS, Washington, D.C. July 23-28, 1995. Reprinted as Application Note 07990995, O.I.Analytical, College Station Texas, 1995. Reprinted in *Water Environment Solutions*, Dec95/Jan96, Vol 2(9):6-9.

while this test takes place. But the check is still worth doing at least once.

The sampling event itself can introduce contamination into sampling. EPA has issued guidance (EPA Method 1669) on how to perform sampling to minimize contamination. It is an involved procedure, requiring at least two sampling technicians, one designated dirty hands and the other designated as the "clean-hands" person. The person designated as clean hands is responsible for all direct contact with the sample and the sample container, while the dirty hands individual is responsible for the preparation and operation of the sampling equipment and machinery and avoids all direct contact with the sample and sample container. In spite of the clean hands and dirty hands labels, both technicians seek to be as clean as possible. This includes the wearing—and frequent changing—of non-contaminating plastic gloves and the wearing of non-contaminating plastic suits.

As mentioned above, dust is a significant source of sample contamination. Dust in the field is just as contaminating as dust in the laboratory. Samples need to be collected in a controlled environment to minimize dust contamination. In the most rigorous sampling events this means collection and manipulation of the sample in an enclosed, dust-free setting. Transportable plastic boxes that are plumbed to a sampling pump for water samples and are provided with positive pressure HEPA filtered air have been found to be quite useful for collection of contamination-free samples.

All parts of the sample container, including the outside must be treated as part of the sample. A sample container that is dirty on the outside can present contamination problems to other samples. For this reason, all samples should be bagged in contamination-free plastic bags. Double bagging can be used to assure cleanliness with the clean hands person placing the sample container in the first bag. Clean hands then places the bagged sample container into a second bag held by the dirty hands technician.

B. Blanks

Blanks are the number one quality control used for monitoring contamination. Various types of blanks are employed in inorganic analysis, including container blanks, field blanks, storage blanks, reagent blanks, sample preparation blanks, calibration blanks, and rinse blanks. Blanks are prepared from analyte-free water; however, they are treated just like samples. In particular, there should be no special handling afforded to blanks, otherwise they lose their value as a quality control.

The reviewer must watch that the units the blank is reported in are the same as those used for the samples. When solid samples are analyzed the laboratory will perform the blank on a target analyte-free portion of water rather than on a surrogate solid such as sodium sulfate or sand. The following example using zinc illustrates the problem. The reported sample result is 5 mg/kg and the associated blank result is 100 ug/L. These values on the surface look like they are a factor of 50 apart. However, there is a significant difference in the sample preparation that these undergo. The blank preparation takes 100 mL water, digests it to 1 mL, then dilutes it back to 100 mL prior to instrument analysis. The soil preparation begins with 1.0 g sample, digests it to 1 mL in acid, then dilutes the digestate up to 100 mL prior to analysis. The blank is correctly reported at 100 ug/L in terms of the 100 mL reagent water that is used as the blank sample but it is not reported in terms of solid. To do this the result must be multiplied by 100 to change the units to those comparable to the solid samples, giving 10 mg/kg. When this is now compared to the sample result of 5 mg/kg the sample result is seen to be due only to blank contamination.

Many persons interpret the result of the blank that accompanies an analytical result as if it were an infallible quality control and the measure of contamination. This interpretation runs something to the order that if the blank is clean then all the

associated samples are clean, or if the blank reveals the presence of contamination, then all associated samples have the same level of contamination. Nothing could be farther from reality.

A blank is a quality control measurement made at one instant of time, at one exact place, and under one unique set of specific conditions. It should be recognized that this set of characteristics of time, place, and conditions is unique and can never be ever repeated. In most situations the blank measures a random event of contamination, the falling of a piece of dust into the sample, the inadvertent touch of a dirty glove, the overlooked digestion beaker during washing, the presence of high levels of the target analyte in the adjacent sample. The only times when contamination can be treated as a systemic event is when it can be definitively traced to a contaminated reagent or acid that is used in the same proportion in all samples, or it is a gas that permeates the air, which frequently happens with ammonia contamination. A further frustrating characteristic of trace metals blanks in a conscientious lab is that in most cases only a single element out of the 20 to 30 target analytes is elevated. A habitually dirty lab will always exhibit blanks with five or more elements at elevated levels in the blank, assuming of course that the blank is performed properly. A clue that laboratory shenanigans may be taking place is the presentation of a pristine blank from an obviously sloppy work area.

The question becomes how to use the blank data to develop meaningful assessments of random laboratory contamination. The answer is to keep control charts. In the days before extensive use of computer systems, control charts were manually prepared and onerous, particularly for a harried technician. Removal of the manual aspects of blank analysis—through automated updating of control charts in the information management system—means that real blank evaluations can be generated on a continuous basis for all analytes. An example is presented in Figure 9-2, where over nine months of zinc blank data from EPA Method 200.7, including a digestion, are illustrated. These data illustrate some powerful interpretational qualities of blank data. First the average for the data is at 11 ug/L with a standard deviation of approximately 13 ug/L. This means that about 2/3 of the data generated in this system are going to exhibit random contamination results at 25 ug/L or below. This is somewhat comforting for samples that exhibit results around 40 ug/L as the level is high enough so that it may be due to zinc actually present in the sample instead of zinc contamination. But it means that a claimed quantitation limit of 20 ug/L is going to be heavily impacted by ambient contamination as most samples that are free of zinc will exhibit false positive levels up to 23 ug/L. A 5 ug/L quantitation limit, while it may be theoretically achievable based on the sensitivity of the instrument, is realistically nonsense.

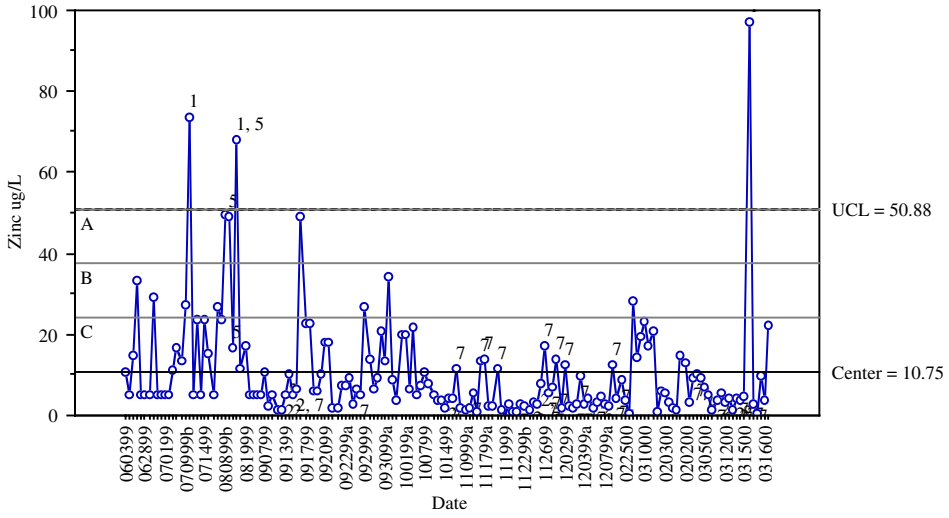

Figure 9-2. Control chart for zinc preparation blanks by EPA Method 200.7.

These considerations are not to imply that an analyte reported as not detected in the analysis needs to be qualified. A non-detect is still a non-detect, unless the laboratory is subtracting the value, average or otherwise, of the blank from that obtained for the sample. In all cases for all analytes: metals, anions, ammonia, *etc.*, the laboratory is not permitted to base results on blank subtraction. The only correct procedure is to report the actual values obtained during the analysis and report the results for the blank, along with any blank statistics. If the data user wants to perform blank subtration, that is their prerogative.

These blank data are always present in labs that follow EPA Methods, as regular performance of blanks is a mandatory aspect of the procedures. The automated preparation and maintenance of control charts for blanks is a rarity. It is to be hoped that it becomes commonplace as it is an invaluable tool for data interpretation and laboratory evaluation.

Data reviewers must be alert to a practice I call blank abuse. This occurs when a laboratory performs an analysis for methylethyl badstuff and gets a blank result of 4 mg/L when the quantitation limit is 5 mg/L. The laboratory reports BDL or <5mg/L for the blank. The blank abuse arises when a sample in the same batch generates a value of 7 mg/L and the laboratory reports it as 7 mg/L without any indication that the associated blank exhibits a similar value. Any reasonable person who is presented with a blank result of 4 mg/L and a sample result of 7 mg/L should suspect that the results are related. If the laboratory does not flag the result with a *B* as potentially being influenced by laboratory contamination, or give some indication to the client that contamination may be responsible for the result, this is where the abuse comes in. The laboratory has allowed the client to make the assumption that the blank is zero, which most clients will do, and misrepresented the sample result as a reliable number.

On the wet chemical side of inorganic analysis, blanks are an integral part of the procedure. Titration blanks are a must to perform. In some procedures, for example the argentometric and mercuric nitrate titrations for chloride found in *Standard Methods* (*SM* 4500-Cl^- B and *SM* 4500-Cl^- C), the Method instructions actually direct the

analyst to subtract the volume required for titration of the blank from that required for the sample. In these cases, the correct procedure is to prepare two blanks, one designed to establish the blank volume, and the other treated as a sample to check the blank volume. It has been noted on occasion that when the two-blank procedure is followed, the blank treated as a sample will generate a negative result. This is an indication that the sample results are being over-corrected. The solution is decidedly not to switch the assignment of which is the titration blank and which is the sample blank, but to find the cause of the difference. One such occurrence should lead the analyst to question the procedure and be alert for future repeats of negative blanks. Several occurrences of negative sample blank results should lead the analyst into abandoning the calculation of sample results based on titration blank volume subtraction as a random rather than a systemic contamination event.

Calibration blanks are routinely used in colorimetric procedures. The intent of the calibration blank is to set the spectrophotometer zero point based on the background absorbance due to the reagents in the test. It is not a calibration point with a value of zero concentration. A second blank should be included in the sample batch even in cases where the calibration blank is processed right along with the samples. This serves as a separate check on contamination, rather than relying on the calibration blank as an automatic correction for contamination. In order to provide the best possible check on random contamination, the second blank should be as far as possible away from the calibration blank in the sample processing order within the batch. Like the titration blank, a duplicate colorimetric blank can read less than zero absorbance, which indicates that random contamination is occurring. This is especially noticeable if the colorimeter has a digital readout that will give a numerical value of the negative absorbance. The older instruments with a needle and scale, such as the very rugged—and still reliable—Milton Roy Spec 20, give only a qualitative idea of how negative the absorbance is.

Electrometric methods of analysis use a blank as a preventative maintenance measure to verify that the electrode can actually generate a zero reading. This special use of blanks is important in techniques that directly convert the electrode output into a concentration. Another determinate of contamination is the initial linearity of the calibration. This evaluation is useful in the situation where systemic contamination has occurred in the reagents. An analyte-free solution can also be processed along with the samples as a contamination check. It is read as a sample, with high readings generally ascribed to the presence of contamination. In techniques such as titrations where the electrode is used to indicate the endpoint of the procedure, blanks are valuable as a quality control on the titration part of the analysis.

A technique used in colorimetric analysis when the individual sample exhibits backgound interference in the determination, such as innate color or turbidity, involves a sample blank. The procedure is to prepare a second portion of the sample that is subjected to the entire analytical procedure, with the exception that the actual color reagent is omitted. The absorbance of this sample blank is subtracted from that of another portion of the sample that has been processed with the color reagent. The difference in absorbances is believed to be that due to the target analyte in the sample, and its concentration is determined by where the absorbance difference falls on the calibration curve. Although widely practiced, the validity of this procedure is somewhat suspect as the sample blank and analytical sample are different in more ways than the simple presence or absence of the color reagent. In most tests the solution containing the substance that reacts with the substrate to form the colorimetric product contains other chemicals that perform one or more of a variety of functions, such as pH control or reduction. Results obtained through use of sample blanks should be regarded as estimates of the true value of the target analyte in the affected sample. A much better approach is to perform a multiple standard addition calibration on the sample.

Storage blanks are used to assess the migration of target analyte from one sample to another during storage. They are particularly important, and the value of the quality control is obvious when the target analyte is volatile, as ammonia. Samples that contain high levels of the volatile analyte are continually releasing it to the atmosphere, especially when the container is not completely sealed. A loose cap on the container is very bad, but even caps that are tight may not achieve a seal due to dirt between the cap and the edges of the mouth of the container. Placing a reagent water filled blank in a container with an intentionally loose cap in the storage area, then analyzing and replacing it every week is an excellent check on contamination in the storage area. If the storage blank is found to be contaminated, all samples with positive results that have been in the storage area since the last clean storage blank are suspected of being contaminated.

A less obvious but no less valuable use for storage blanks concerns analytes that are not volatile. In this context the contamination moves from one container to another *via* the analyst's hands and gloves. Most sample containers, unless bagged or double bagged, are contaminated on the outside. All laboratory technicians have encountered sample containers that are caked with dirt, mud, oils and grease. As the analyst physically touches and moves samples in the search for the correct container needed for a particular analysis, they spread the grime around. A reagent water filled container with an intentionally loose cap is placed on each shelf in the storage area, and every time an analyst moves samples on that shelf, they also pick up and move the storage blank. This blank is replaced and analyzed for a random selection of common contaminants such as iron, chloride, sulfate, and aluminum at regular intervals. Although the solution inside the storage blank will only occasionally reveal contamination, it serves the important purpose of making the analysts aware of contamination on their hands and gloves. Some analysts have the habit of using gloves only to protect their hands. Clean gloves are also a key factor in the prevention of sample cross-contamination. Gloves need to be changed often and especially after a dirty container has been handled. Seeing grimy glove prints on the outside of the storage blank can be just as informative as positive hits obtained from the contents of the container.

Rinse blanks are used in all situations where the analytical instrument draws a sample inside it for determination. They are required periodic controls for FLAA, GFAA, and ICP instruments, but are also valuable for procedures that use an ion chromatograph, capillary electrophoresis instruments and colorimetric systems that have flow-through cells. The rinse blank at a minimum must be analyzed immediately after the completion of calibration before the first analytical sample is drawn into the device, and at the completion of the run after the last sample is analyzed. Further confidence is obtained by analyzing a rinse blank after every 10th sample. Ideally a rinse blank should read zero, with a permitted range of plus and minus the instrument detection limit from zero. Readings outside this range should lead the analyst and the data reviewer to suspect that all samples processed since the last acceptable rinse blank have been affected. A positive rinse blank means that detected analytes in the samples may be biased high in the results and are thus evaluated as estimates. Samples with results indicating that the target analyte(s) are not detected are reliable. If a rinse blank has a negative result, all samples with positive results are suspected of being biased low and the reported results are low estimates, while samples with results indicating that the target analyte(s) are not detected are unreliable.

Blanks are also useful for assessing non-target analyte contamination. The information is not generally available in procedures that are dedicated to the determination of set analytes such as titrations, electrode determinations, colorimetric determinations and instrumental methods such as FLAA, GFAA, and ICP-AES with fixed configurations. However, techniques that use a chromatography-like separation,

such as ion chromatography and capillary electrophoresis, or employ a multi-analyte scanning capability, such as X-ray fluorescence spectrometry, ICP-MS, ICP-AES with a PDA, or anodic stripping voltametry, possess the ability to assess non-target analyte contamination. The analyst should attempt to identify the contaminant whenever possible. A note should be made in the instrument log of the presence of the non-target analyte contaminant and its suspected identity. If the contaminant is found to re-occur, efforts need to be made to eliminate it from the analysis.

C. Other Indicators of Contamination

Blanks are not the only quality control tools that can be used to assess laboratory contamination. Any time a sample or standard is analyzed in duplicate this provides an opportunity for a contamination check. Useful duplicates include sample duplicates, matrix spike duplicates, and laboratory control sample duplicates.

Sample duplicates are probably the best source of alternate information on contamination in inorganic analysis, but the data must be evaluated with due consideration of the innate precision of the particular test. The situation frequently occurs where one member of a duplicate pair is reported with a positive value for the target analyte while the other member is reported with a Below Detection Limit (BDL) or a non-detected result. For example the two results might be 11 mg/L and BDL with a detection limit of 5 mg/L. Applying the laboratory's quality control acceptance limit of say 10 for RPD to this situation is going to mislead the data reviewer into suspecting that these data are indication of laboratory contamination. It should be remembered that RPD expectations are never determined near the detection limit, rather a spike concentration that is near the mid-point of the calibration curve is normally used, thus the RPD range is not a reliable guide here. The Method Detection Limit is a measure of precision at low levels; however, it is determined using spiked samples of reagent water that are completely lacking in the normal variations that are seen in real samples. A good rule of thumb to follow for water samples is to apply a window of ± 3 times the MDL to the results, then see if the values fall within each others' window. In this example the windows are 11 ± 3 x 5 giving <5 to 26 and 5 ± 3 x 5 giving <5 to 15. These windows exhibit substantial overlap and the value of 11 falls in the <5 to 15 window, while the BDL result falls in the <5 to 26 window. Thus the conclusion in this case should be that the values of 11 and BDL are within expected variance and not indicative of contamination.

In contrast let's suppose that the reported values are 25 and BDL with a detection limit of 5 mg/L. The respective windows are 10 to 40 and <5 to 15. These ranges exhibit only minimal overlap and, further, the reported values are both outside the expected variation of the other value. Thus the proper conclusion here is to suspect possible laboratory contamination.

If the duplicates are derived from a soil or other solid sample, the lack of sample homogeneity may lead the data evaluator to use a somewhat wider range for the expected variations. However, an initial comparison of ranges that are generated from the value ± three times the detection limit should be tried. It is often found to work. If a wider range is needed, say up to ± five times the detection limit, the data may be within the expected range of variations; however, the reviewer may want to find out something about the physical state of the sample and the laboratory sample handling practices to help with the evaluation. The difference in this case of comparing sample duplicates and the following discussion of field duplicates, is that laboratories are expected to be making significant efforts to homogenize solid samples, thus sample duplicates should be very similar. If the laboratory practice is to simply spoon two aliquots out of the sample container to prepare the duplicates, then larger variations in results due to the sampling practice can be expected. Large variations in duplicate

results may not indicate laboratory contamination but rather poor laboratory aliquoting technique. This possibility should be mentioned in the reviewer's report of the data evaluation.

Field duplicates are samples from the same area that are separately containerized by the people doing the sampling in the field. If the sample is well mixed by the technicians and the homogenized sample split prior to placement in the containers, then the laboratory results of field duplicates can be evaluated for contamination in much the same manner as that used for sample duplicates. However, if the field duplicate is actually a co-located sample (in other words, the individual samples in the duplicate are separately spooned into containers from the same hole in the ground without mixing), then greater variability in the results can be expected. Although the results from each of the samples in the duplicate pair can be examined with an eye toward revealing contamination problems, there is difficulty in determining what is contamination and what is normal variation. Further in the event that contamination is believed to have occurred, specifically attributing the source of the contamination to either the laboratory or the field is problematic.

Equipment blanks and field blanks are useful for detecting contamination that is due to sampling practices used in the field operations. Equipment blanks should not be limited to just the backhoes, shovels, augers, spoons and other tools used in the field operations, but should include rinses of the gloves that the technicians are using.

Although matrix spike duplicates and laboratory control sample duplicates are good ancillary tools for detecting laboratory contamination in organic analysis, they have limited utility for this purpose in inorganic analysis. This is largely due to the spiking solutions generally containing all of the analytes that are the target of the analytical procedure. This is not to say that these quality controls are not useful for evaluating non-target analyte contamination in the multi-analyte techniques. In this regard they can admirably help to identify whether non-target analyte contamination is random or systemic and also help give a quantitative estimate of the extent of the contamination.

D. Conclusion

All laboratories have contamination problems. These problems are unavoidable and largely insurmountable without significant investment in construction and maintenance of clean room facilities. The laboratory must have an active program designed to continuously monitor the many different types and sources of contamination. When contamination is found, active steps must be implemented to remove or minimize the contamination. In the absence of a vigorous contaminant minimization and monitoring program, laboratory results are always suspect.