

PROBLEMS IN THE LABORATORY

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Implementation of the regulations we have been discussing today will depend upon reliable chemical analyses. In fact, the whole Safe Drinking Water Act hinges on the ability of analytical personnel to consistently day after day obtain reliable results. Without good analytical data, the regulations cannot be enforced and without enforcement the regulations are worthless. Reliable data is also critical in terms of keeping costs down, since systems in violation must repeat analyses and public notification is required of systems in violation. Reliable data is also necessary for technical operations and long range planning. And, of course, reliable data is necessary to protect the public health and peace of mind. (Data which is in error by being too low can endanger the public health, and data which is in error by being too high can unnecessarily alarm the public).

What then is involved in obtaining consistent reliable results? The first concern is sampling. The chemical analyses will be only as good as the sampling. The sample must be taken in such a manner that no contaminants are added and the constituents which are sought are not lost. Complete preservation of samples is a practical impossibility. At best, changes can only be retarded. Changes can occur because ions may precipitate, change valence state, dissolve, volatilize, form complexes, be adsorbed onto the container surface or exchange ions with the container surface. Changes can also occur because of biological action. Soluble constituents may be converted to organically bound material, or cell lysis may result in release of cellular materials into solution. There is no one method of preservation which will retard all types of changes. Decisions must be made in advance of sampling as to the desired constituents and the method of preservation. Sometimes several samples are taken and several methods of preservation employed. A satisfactory sample must also be a representative sample. It must reflect the total water. A decision needs to be made as to whether to use glass or plastic containers, add acid or whether the sample is going to be heated or cooled. It is impossible to give directions covering all conditions so sampling must be at least supervised by qualified personnel. In general, the shorter the time between sample collection and analysis, the more reliable the results. Qualified personnel are going to be needed and this is not college students, colleges are more interested in teaching theory. We are going to need on the job training to be qualified and this will be a problem in New Mexico.

In the chemical laboratory, the water and chemicals must be of high quality and free of trace contaminants. Ordinary tap water obviously isn't good enough and must be distilled. The best type of still is all glass, which is three or four times more expensive than a metal still. Many laboratories use metal stills because they are cheaper but water distilled in a metal still contains metal ions, which must be removed by ion exchange columns. Distilled-deionized water will still contain dissolved carbon dioxide which may have to be removed by boiling. The chemicals used in the various assays must be of the best quality. This has always been important but now when analyses extend into the ppb range, it is an absolute must. Many times this necessitates further purifying the chemicals in the laboratory or buying specially purified chemicals and there is a difference between companies as far as chemical purity is concerned. Either way it adds to the cost.

All glassware must be scrupulously clean. Having the glassware clean enough to eat off of isn't good enough. It must have no trace contaminants absorbed to the sides of the glass. This is important again because of the very trace amount being sought. For biological assays the glassware must be sterilized and if taken into the field must be kept sterile. Another problem with dirty glassware is that it not only causes contamination but also inaccurate measurement. A dirty pipet won't deliver the volume of liquid it should. When you are working with very small amount, being off a drop or two is very important.

The best method of analyses in each particular case must be decided upon. The decision must be based on the degree of accuracy required, the expected concentration of the desired constituent, the interferences which may be encountered, the amount of time required for analysis, the established validity of a method and the skills and equipment required.

The analyst must also keep in mind the fact that an element in the presence of others may behave quite differently than when it is by itself. There is no problem finding methods of sufficient sensitivity for the determination of elements when they occur alone. The rub comes in because elements never occur alone in water and further more in the case of analyses required by the Safe Drinking Water Act one is expected to determine small amounts of an element in the presence of very large amounts of other elements.

Before analysis, all forms of the element must be converted to the same form. This is extremely important and is the point where the technicians are separated from the analysts. This is one of the problems with the selenium analysis. In the case of mercury analysis all forms of organic mercury must be carefully converted to inorganic mercury in the +2 valence state before analysis is attempted. This must be done without losing any mercury which is difficult since mercury is volatile.

Any expected interferences must be removed before analysis or corrections must be made for them. An alert analyst is constantly asking himself (herself?) "What interferences may be expected?" "How can they be corrected for?"

Adequate standards are a necessity. Two types of standards are needed. An external standard, to standardize the reagents and/or equipment. This usually consists of a standard curve, various amounts of the element in distilled water. The internal standard generally consists of a known amount of the element in the same matrix as the sample. This is the difficult standard to obtain since the major constituents in the water sample aren't likely to be known and would be expensive to determine and duplicate for each sample. A method of handling this problem is by spiking an aliquat of each sample with a known amount of the element in question. This is called the "Method of Additions". One precaution that should always be observed if possible is that the added known be in the same chemical form as the unknown. This isn't always possible and is another reason why care should be taken before the analysis to convert all forms of the element to the same form. The known amount should always be added at the beginning of an analysis. This aids the analyst in being sure that the known is in the same chemical form as the unknown and will also help the analyst account for any losses. An analysis where this is particularly important is the analysis of mercury. Even so the "Method of Additions" can't correct for every type of interference. In the case of atomic absorption analyses, for instance, it won't correct for "non-molecular" absorbance.

The analyst must now consider the accuracy of his result. There is a wide misunderstanding as to the accuracy of results obtained in analytical work, and also a confusion between precision and accuracy. A useful concept here is that of a target. Three shots that are clustered at one side of the target are precise, but not accurate. Conversely, shots clustered about the bullseye are accurate. Precision can be easily established, but it is extremely difficult to judge accuracy, since in chemical analysis the "real" answer is never known. How then is the most probable value established? This is only safely done by carefully determining the constituent by methods that differ from each other as much as possible. This obviously is extremely costly, and not necessary for routine monitoring, provided that the method being used has been shown to be reliable. However, in the case of a disputed analysis, it is the way to establish the most probable value. Another misunderstanding exists as to the term sensitivity. Sensitivity refers to the degree of response received for a certain amount of an element and in no way implies accuracy. Consider the emission spectrograph, for example, it is highly sensitive; copper in a solid can be determined to 1 ppm or less, but the results have an accuracy of ± 50%.

The National Interim Primary Drinking Water Standards list maximum contaminant levels for 22 parameters, including trace inorganics, trace organics and radioactivity. E. P. A. has certified to Congress that these maximum contaminant levels are analytically obtainable, which doesn't necessarily imply accuracy. What this means is that an analyst with sometimes very expensive equipment (under the best conditions) who is very familiar with that particular assay can reach those certified limits in a sample containing distilled water and the element of interest. This is different from "real world" conditions, where an analyst is responsible for running many different assays on the least expensive, most practicable equipment in solutions that vary from low T. D. S.

(total dissolved solids) to high T.D.S. In New Mexico not only does the T.D.S. vary but can range from high sodium chloride-low calcium sulfate to high calcium sulfate low-sodium chloride, to high calcium bicarbonate-low sodium sulfate and all variations in between. The colloidal content of New Mexico waters is also very high. The minor elements can range all over the place and the analyst is looking for trace elements at the ppb range.

As far as New Mexico is concerned there is going to be a problem with having adequate laboratories. Of the 22 parameters, 4 could be routinely determined by a trained technician using relatively inexpensive equipment, the others require either highly trained personnel or expensive equipment or both.

The Safe Drinking Water Act specifies that analyses conducted for the purpose of determining compliance must be done by a laboratory approved by the entity with primary enforcement responsibility (E.P.A.). The E.P.A. has already certified the HSSD state laboratory. However, this laboratory won't be able to handle the volume of analyses required and for the biological assays, many communities are too far away to be able to send assays to the state lab. As far as I have been able to ascertain, there is at present only one other laboratory in the state which has the capabilities of determining all the parameters and could be certified.

Cost is another problem. The average cost of analyzing water for drinking water requirements is going to cost about \$200.00 a sample, and this doesn't include sample collection. Especially for the smaller communities this is going to be expensive.

Finally, what happens when there is a disagreement between discharger and certifying agency as to the exact level of a contaminant? I don't see any provision in the Act which covers this problem.

The regulations specify the procedures to be followed in analyzing samples for each of the maximum contaminant levels. This is fine but it doesn't necessarily assure reliable results. This is what I have been trying to emphasize this afternoon, that reliable results depend on a multitude of things. The analyst must be concerned about sampling, labeling of samples, storage of samples, the quality of the chemicals and distilled water, about glassware, about maintenance of equipment, the analytical method itself, any expected interferences, adequate standards, accurate mathematical computations and proper recording of the data. Carelessness at any point can negate the complete analysis.

There appears to be an assumption on the part of Congress, E.P.A. and even the general public, that the analyses of the maximum contaminant levels is going to be cut and dried, that the "real" amount of a contaminant will be readily determinable. This assumption is wrong, could cause confusion and alarm, endanger the public health by causing a false sense of security, and in any case will be costly.