C. QUALITY ASSURANCE

by David L. Smith, CIH; Michele L. Bolyard, CIH; and Peter M. Eller, Ph.D., CIH

Contents: Page

1. ROLE OF LABORATORY QUALITY ASSURANCE PROGRAM

Analytical data are used to make a variety of decisions, i.e., to decide whether a particular chemical agent is present in a workplace atmosphere, whether a hazard to workers' health exists in that atmosphere, or whether a workroom atmosphere complies with applicable standards. Errors in such data can have a variety of costly effects [1]. The consequences of erroneous data may lead to the wrong decision being made as to whether a non-compliance situation exists. If the analytical results are a part of a larger experiment, perhaps the wrong conclusion might be reached or the results might be uninterpretable. If the presence or absence of a particular agent is erroneously reported, a threat to workers' health may be allowed to continue. It is the role of a laboratory's quality assurance program to provide the necessary safeguards to minimize these occurrences and to provide a means of detecting errors when they do occur. There are many good texts and articles addressing the subject of laboratory quality control [2,3,4,5]. The purpose of this chapter is to address some of the

aspects of quality control as they relate to industrial hygiene laboratory quality control.

It is not possible to design a quality assurance program to fit all laboratories since no two laboratories serve the exact same purpose or operate in exactly the same manner. Each laboratory must set its own operating procedures and quality control practices, and document them in a Quality Assurance Manual [2,3,5]. This chapter, therefore, will not set forth concrete recommendations for implementing a quality assurance program, but rather will present aspects of laboratory quality assurance and quality control which should be addressed by each laboratory.

A successful quality assurance effort cannot be achieved through the efforts of only one individual. A laboratory's quality assurance coordinator needs the assistance and cooperation of all laboratory personnel to be effective. To this end, it is necessary to discourage adversarial relationships between quality control personnel and bench chemists. Analysts must be trained and made aware of the purpose and value of quality assurance functions and, in turn, the quality assurance program must be designed so that its functions are based on sound goals directed toward improving the performance of both the individual analyst and the laboratory as a whole.

Frequently, analytical results are challenged months or years after the analysis is complete. In order to support the original data, an effective, complete, record-keeping system must be maintained. Another chemist must be able to reconstruct the exact treatment to which the samples were subjected solely from a laboratory's records. Furthermore, if the appropriate quality control checks were performed with the analysis and documented, there can be no doubt regarding the results.

2. ORGANIZATION

A laboratory, just as any other organization, should have a clearly defined organizational structure. Responsibilities of each member of the laboratory staff should be in writing and understood by all. In this way, confusion regarding tasks which need to be performed can be avoided.

The specific organizational structure of the laboratory will vary, depending on the laboratory's function. Two functions which relate to quality assurance should be assigned in every laboratory: the quality assurance coordinator and the sample clerk. The size and nature of the laboratory may preclude assignment of a full-time position to these functions; however, a laboratory member should be assigned these duties and it should be understood that they are to have top priority.

a. Quality Assurance Coordinator

The quality assurance coordinator's functions will depend on the size and nature of the laboratory. This professional has overall responsibility for assuring that reported data meet established standards for precision and accuracy and that these results can be supported scientifically by the various quality control checks performed with the analysis. One of the major functions of this individual is to perform audits of the quality control system and to implement changes that eliminate recurring errors

[2,3,4,5]. The quality assurance coordinator should not be under the direct supervision of management responsible for day–to–day laboratory operation. In this way, conflicts between the laboratory's dual responsibilities of providing analytical results in a rapid fashion while maintaining quality can be avoided. The quality assurance coordinator should also serve as a resource person

for chemists or managers on questions or problems related to quality assurance and should have a working knowledge of statistics, including quality control charting, and experimental design.

b. Sample Clerk

The sample clerk's functions will also vary, depending on the size and function of the laboratory. As a minimum, the sample clerk is responsible for the receipt and log–in of samples. Field samples should be stored in a secure location under proper conditions (temperature, etc.) until analysis. Logging and tracking of samples in the laboratory is important so that the history of these samples can be documented and processed in a timely manner. The sample clerk may also be given the responsibility of maintaining chain of custody documentation.

3. QUALITY ASSURANCE IN SAMPLING

Quality assurance procedures should not be overlooked by personnel performing field sampling. The field sampling parameters often have more effect on precision and accuracy of the final result than parameters of the measurement [2,4,5,6,7]. Field personnel should become familiar with sampling and measurement methods which they will use. The methods usually specify the proper sampling media to be used, the correct flow rate and sample volume, as well as special precautions on sample handling, shipping and possible interferences.

Sampling equipment must be maintained in reliable working order. It is desirable to have one person or group given responsibility for the care, maintenance and stocking of field sampling equipment. This person or group should periodically inspect and repair all equipment and keep track of the use and location of sampling equipment when it is signed out. Sampling pumps should be calibrated with each use. This calibration should be performed with the sampler in line. Since differences in pressure drop across the sampler will affect flow rate, it may be necessary to perform the calibration with the actual sampler to be used.

The exact sampling time must be known in order to accurately estimate the sampled volume. Recording only the start and stop time assumes that the pump functions properly over the entire sampling period. Occasional spot checks for proper operation should be made throughout the sampling period.

Since many modern analytical techniques are extremely sensitive, special care must be taken to avoid contamination of field samples [8]. Samples must not be stored or shipped with bulk materials which

might spill or otherwise present the possibility for contamination. The glassware or other containers used in sampling and shipping should be subjected to any cleaning procedures recommended in the analytical method.

Careful record keeping in the field is also important. Pertinent information such as temperature, humidity, possible interfering compounds, sampling location, etc. should be documented. Special care should be taken in sample labelling and in preparation of paperwork accompanying the samples so that confusion in the laboratory is avoided.

Field blanks are used to estimate contamination which may occur immediately before and after sampling, during shipment, or while awaiting measurement in the laboratory. The nature and number of blanks taken will depend on the method and sampling situation; therefore, field sampling personnel must attempt to determine what sources of contamination are possible in the specific situation at hand. The field blank strategy must then be designed accordingly. Where possible, a written sample protocol should be developed before actual sampling begins [3,4,9,10]. The protocol should contain a description of the environment being sampled; the assumptions made in derivation of the model of that environment; when, where, and how the sampling will be done; and how many samples will be taken. Samplers should be identified by batch or lot number of sampling media.

4. QUALITY ASSURANCE IN MEASUREMENT

Certain quality control checks should be performed with each sample set [2,4] to further support the reported results on actual field samples. The exact number and nature of these checks depend on the specific method and circumstances under consideration and should be thought of as an integral part of the method itself (i.e., a measurement should not be considered completed without the quality control checks also being completed). Each analyst must take an independent responsibility for assuring that the analytical quality control system works. This can be accomplished by using known spiked samples which closely simulate field samples with regard to concentration and interferences. Since the analyst is most familiar with the methods being used and should know what range of recoveries to expect, problems with the system can be detected early. We will attempt to recommend specific quality control checks to be performed with the methods in NMAM; however, our recommendations cannot be expected to cover all situations. The user of these methods should consider adding additional quality control checks as appropriate.

a. Methods

First, and perhaps most important in the area of quality control, a laboratory must have adequate measurement procedures. These methods should be written so that there is no doubt in the analyst's mind of the exact steps which must be performed and so that future references to the work can be as exact as possible. The methods used should be evaluated, where possible (either by the laboratory itself or by some other organization), to verify that the methods perform satisfactorily. Factors which could be evaluated include the recovery of the analyte of interest from both spiked samples and

generated samples, the stability of collected samples or possible interferences to accurate use of the method. Methods should be tested for ruggedness so that critical steps in the analysis can be identified. Experimental designs have been published which permit rapid evaluation of a number of factors involved in the analysis (e.g., [11]).

b. Standards

Standard solutions may be for either identification or quantitation of the analyte of interest. The bulk material used for preparation of standards should be of sufficient purity to avoid errors in the identification or quantitation. Where available, Standard Reference Materials (SRMs available from the U.S. National Institute of Standards and Technology) or other well-characterized standards are useful for assuring that results are consistent with other organizations and agencies [3]. Laboratory reagents and standards should also be properly labelled with contents, and receipt and expiration dates.

For quantitation, sufficient numbers of standards should be prepared so that adequate confidence intervals on reported values can be obtained [3,12]. As a guideline, we recommend that calibration curves be prepared with triplicate points at each of at least five different concentration levels. The standard curve should be prepared so that linearity can be assured over the range of the curve. Also, it is important that the concentration of standard solutions be chosen to bracket the actual samples. In this way, extrapolation outside the range of standards is avoided. The concentration of standard solutions should be chosen to be consistent with the purpose of the sampling. That is, if it is desired to demonstrate whether exposure standards are being met, then the standard curve should be constructed to bracket the concentrations which would be encountered at or near the applicable exposure standard. If it is desired to demonstrate whether a compound is present in the atmosphere being sampled, then the calibration curve should be constructed closer to the limit of detection. During measurement, working standards should be interspersed with field samples. In this way, it should be possible to detect if instrument drift becomes significant. Internal standards are useful for correcting instrument response for the actual amount of sample injected into a chromatograph. The internal standard should be chosen so that its retention time is reasonably close, without peak overlap, to the peak of interest.

c. Blanks (also see page 26)

A particular analysis may involve several types of "blank" measurements including reagent blanks, media blanks or field blanks. Reagent blanks measure the signal contribution from solvents, acids or other reagents used by the laboratory in preparing samples for analysis. Media blanks measure the signal contribution from the collection media (impinger solution, filter, sorbent tube, etc.) and field blanks measure signal contribution of the media plus any contamination which may have occurred during handling, shipping and storage before analysis. The nature and number of blank measurements will depend on the method and circumstances, but the purpose of all blank measurements is to help prevent errors in identification and quantitation of field samples [3].

d. Blind Samples

Blind samples are prepared by someone other than the analyst performing the measurement and are to provide an independent check on the accuracy and precision of the measurement.

If blind samples cannot be prepared with confidence, their use should be avoided. In these cases, confusion may result when discrepancies occur and it will not be possible to say for certain whether the measurement or the blind sample was in error.

The results should be used in conjunction with control charting techniques to identify errors or malfunctions in the system [2,12,13]. To accomplish this goal, quality assurance

personnel should work closely with laboratory personnel to quickly identify and eliminate trouble spots.

It will not always be possible to isolate the source of error in the results of a blind sample. In these instances, it should be recognized that it will not be possible to defend quantitative results for that particular sample set; therefore, reporting of results where these discrepancies occur should be avoided.

e. Recovery Studies

Recovery studies should be performed as a part of the measurement whenever the analyte of interest must be liberated or separated from the sampling media. The analyte of interest should be added to the media at levels consistent with the field samples. These "spiked" samples should then be treated in the same manner as the field samples. Corrections for recovery should be made whenever the measured recovery is significantly different from 100%. Even if recovery has historically been 100%, recovery studies can be useful as additional analytical and calculation checks. It is often helpful for a laboratory to maintain a record of past recovery studies so that current data may be compared for discrepancies. Samples for which estimated recovery is less than 75% should be reported as "semiquantitative."

f. Duplicates

Duplicate preparations of bulk materials are useful as an indication of the uniformity of the bulk material. Duplicate injections or measurements from air samples are of lesser importance since preparations from air samples are generally fairly uniform in nature. True duplicates of air samples are useful as an indication of both the reproducibility of the entire sampling and measurement method and as an indication of the uniformity of the atmosphere being sampled.

5. INTERLABORATORY TESTING

Assignable analytical uncertainty can be considered as consisting of interlaboratory and intralaboratory

variability. A knowledge of the magnitude of these two sources of variability is essential in order to interpret and use analytical data properly. Intralaboratory variability can be estimated from the results of analysis of blind samples. Interlaboratory testing requires the cooperation and coordination of a number of independent laboratories [2,11].

Interlaboratory testing can also be useful for defining the relationship of data reported by different laboratories using either the same or different measurement techniques [12,15,16]. Participation in such studies can be useful for uncovering errors in methodology or identifying critical steps in the procedures.

The Proficiency Analytical Testing (PAT) Program operated by the American Industrial Hygiene Association in cooperation with NIOSH is useful for measuring a laboratory's performance on a variety of common industrial hygiene samples, including solvent vapors

on charcoal tubes and metals, asbestos and silica on filters. Participation in this program by laboratories performing industrial hygiene analysis is strongly encouraged.

Similarly, the American Industrial Hygiene Association (AIHA) operates a laboratory accreditation program for industrial hygiene laboratories. Site visits and application reviews can provide a useful review of a laboratory's overall quality assurance system, as well as the adequacy of personnel, facilities and equipment. Appendix E of [2] lists over twenty other proficiency and check sample programs. An extensive listing of laboratories accredited in specific test protocols is also available [17].

6. REPORTING

The detail and nature of the analytical report will depend on the function of the laboratory. As a minimum, the report should include a description or reference to the method used, any deviations or special circumstances encountered with the sample set, estimates of the limits of detection and quantitation, the date of analysis, as well as the results themselves. The report should be signed by the analyst and at least one other person who is responsible for approving the report. The laboratory should adopt a standard report format and attempt to maintain that format with all reports.

The limit of detection (LOD) is defined as the amount of the analyte which can be distinguished from background. The limit of quantitation is that amount of analyte above which the precision of the reported results is better than a specified level. There are numerous methods of determining these quantities and many opinions as to which method is correct. The laboratory should decide on a method for determining these quantities and be consistent to the extent possible in its use. In NMAM, the American Chemical Society definition of LOD (i.e., a sample giving a signal three times the standard deviation of background) is used [4,18].

Sample data should be corrected for recovery or desorption efficiency and for reagent and media blank

response. However, field blanks should be treated like field samples (corrected for reagent blanks, media blanks, and recovery). If correction for contamination in the field blanks is necessary, this correction should be performed by the person who submitted the sample.

Data should be reported simply and concisely and in a manner that "their meaning is not distorted by the reporting process [4,12,13]." Attention should be given to the number of significant figures reported. Generally, only the last figure reported should be in doubt.

7. LABORATORY NOTEBOOKS

Laboratory notebooks are used for recording all experimental and analytical notes and data [19]. New notebooks should be logged out to a chemist. The notebook remains the property of the laboratory and should be kept in a central location by the laboratory after it is filled.

Notebooks used in the laboratory should be hard-covered and bound. Use of notebooks with removable pages (e.g., loose-leaf notebooks) should be discouraged. The pages of the notebook should be numbered and any entries made by an individual other than that to whom the book was assigned should be noted. Some laboratories require that the individual notebook pages be signed by the chemist for legal reasons.

The notebook should contain all information gathered by the chemist pertaining to the sample. Where appropriate, lab number, field number, sequence number and other identifying numbers are noted. Measurements requested, identification of the method, modifications to the method and the sample originator should be included. A description of the sample (whether bulk material, charcoal tube, etc.) should be included. Data on quality assurance aspects of the sample set such as blank values, recovery studies and duplicate determinations should also be included. Formulae used to calculate results and a sample calculation should be shown.

If permanent retention of computer printouts, recorder charts or similar items is deemed necessary, they should be pasted, taped or stapled in the notebook, if practical.

The minimum data entered in the notebook should be sufficient to enable another chemist to derive the same results as the original worker, with no other source of information. In addition to this minimum data, any other facts appropriate and pertinent to the sample analysis are to be entered.

A chemist's notebook is always subject to inspection by his colleagues, supervisors or inspectors from outside the laboratory. Therefore, it is imperative that the notebook be maintained in a professional manner and contain all pertinent information that may be required by other parties, regardless of the particular importance of that information to the chemist. Furthermore, the notebook must be maintained in such a manner that it can withstand challenges as to the validity, accuracy or legibility of its contents.

8. INSTRUMENT MAINTENANCE

Laboratory instrumentation must be maintained in proper operating condition. We have found that in numerous cases the cause for out-of-control quality control samples has been traced to faulty instrument performance. In many of these instances, the operator was unaware that instrument performance had degraded. Performance checks can be useful in documenting instrument performance over time and in detecting deviations. To be of use, performance check procedures should be quick and easy to perform. Appendix C of [2] gives details of suggested performance checks for a variety of instruments. Where appropriate (e.g., balances, microscopes) periodic calibration should be performed and documented. Records of calibration should be recorded in the logbook for that instrument.
An instrument's maintenance history is often valuable in troubleshooting problems with that instrument. The record of instrument maintenance should be maintained in an "instrument logbook" and kept near that instrument or in a recognized location.

Service contracts or maintenance agreements for instrument repair are useful for assuring that instrumentation is serviced by qualified personnel and maintained in proper operating condition.

9. SAMPLE TRACKING

A laboratory should have a mechanism for logging and tracking samples after they are received in the laboratory so that all samples can be processed in the most efficient manner. The exact system used for sample tracking will depend on the size and nature of the laboratory and may range from hand-entry logbooks to sophisticated computer-based systems. The system should include a means of cross-referencing laboratory sample numbers with field sample numbers and it should be possible to determine the chemist, instrument, and other aspects of the sample set from the field number.

Sample tracking systems may also be used to produce management statistics which may aid in forecasting future sample loads or point to problem areas in sample turn-around.

10. QUALITY ASSURANCE RECORDS

Maintenance of quality assurance records aids in recalling details of a particular analysis at a future date. A condensation of quality assurance data can be used as supporting evidence to field personnel should the need arise. Quality assurance records can also be used to track various quality assurance parameters over time (such as desorption efficiency or blank values).

Computerized recordkeeping systems should be backed up periodically. Archive copies of computer data require specialized storage conditions and these archive copies may not be reliable for extended periods of time.

Filing of records should be current and accurate. If rapid retrieval of data is not possible, then

maintenance of quality assurance records loses its purpose. The primary purpose is to provide a system to furnish information rapidly regarding the status of specific sample sets.

11. REFERENCES

[1] Hunter, J. S. "The National System of Scientific Measurement," Science, 210, 869 (1980).
[2] Garfield, F. M. Quality Assurance Principles for Analytical Laboratories, Association of Official Analytical Chemists, AOAC International, Arlington, VA (1991).
[3] Taylor, J. K. Quality Assurance of Chemical Measurements, Lewis Publishers, Chelsea, MI (1987).

[4] Keith, L. H. Environmental Sampling and Analysis: A Practical Guide, Lewis Publishers, Chelsea, MI (1991).
[5] Dux, J. P. Handbook of Quality Assurance for the Analytical Chemistry Laboratory, Van Nostrand Reinhold, New York (1986).
[6] Kratochvil, B. and J. K. Taylor. "Sampling for Chemical Analysis," Anal. Chem., 53, 924A–938A (1981).
[7] Cali, J. P. and W. P. Reed. Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis, NBS Spec. Publication 422, Vol 1, 41 (1976).
[8] Kosta L. Talanta, 29, 985–992 (1982).
[9] Leidel, N. A., K. A. Busch, and J. R. Lynch. Occupational Exposure Sampling Strategy Manual, U.S. Department of Health and Human Services, Publ. (NIOSH) 77–173 (1977).
[10] Leidel, N. A. and K. A. Busch. Statistical Design and Data Analysis Requirements, Chapter 3 in L. V. Cralley and L. J. Cralley, Eds., Patty's Industrial Hygiene and Toxicology, Vol. III, 2nd Edition, Theory and Rationale of Industrial Hygiene Practice, John Wiley & Sons, NY (1984).
[11] Youden W. J. and E. H. Steiner. Statistical Manual of the Association of Official Analytical Chemists, AOAC, Washington, DC (1975).
[12] Taylor, J. K. Statistical Techniques for Data Analysis, Lewis Publishers, Chelsea, MI (1990).
[13] Kelley, W. D., T. A. Ratliff, Jr., and C. Nenadic. Basic Statistics for Laboratories – A Primer for Laboratory Workers, Van Nostrand Reinhold, New York (1992).
[14] Horwitz, W., L. R. Kamps, and K. W. Boyer. "Quality Assurance in the Analysis of Foods for Trace Constituents," J. Assoc. Off. Anal. Chem., 63, 1344–54 (1980).
[15] DeVoe, J. R., Ed. ACS Symp. Ser. No. 63, American Chemical Society, Washington, DC (1977).
[16] Shulman, S. A., J. H. Groff, and M. T. Abell, "Performance of Laboratories Measuring Silica in the Proficiency Analytical Testing Program," Amer.Ind.Hyg. Assoc.J., 53: 49–56 (1992).
[17] American Association for Laboratory Accreditation, A2LA 1993 Directory of Accredited Laboratories, Gaithersburg, MD (1993).
[18] NIOSH/DPSE Standard Operating Procedure, "SOP018 Limits of Detection and Quantitation," Cincinnati, OH (1991).
[19] Kanare, H. M., Writing the Laboratory Notebook, American Chemical Society, Washington, DC (1985).