FINAL REPORT

QUALITY CONTROL AND ASSURANCE APPLIED TO THE
ANALYSIS OF ENVIRONMENTAL SAMPLES COLLECTED
FROM KNOWN GEOTHERMAL SITES

MASTER

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ABSTRACT

The components of an analytical quality control and assurance program for the analysis of trace toxic and priority pollutants are reviewed in general. It is recommended that these principles be applied to develop increased confidence in a laboratory's analytical accuracy by establishing validated standard operating procedures with built in controls and internal cross checks and developing an approved standard operating procedure for quality assurance consisting of audits and appropriate documentation. It is also recommended that interlaboratory comparisons be considered as a means of continually documenting analytical accuracy.

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QUALITY CONTROL AND ASSURANCE APPLIED TO THE
ANALYSIS OF ENVIRONMENTAL SAMPLES FOR TOXIC
AND PRIORITY POLLUTANTS

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INTRODUCTION

It has often been said that an analysis is only as good as the sample on which it is performed. In fact, Thiers recommends that "... unless the complete history of any sample is known with certainty, the analyst is well advised not to spend his time analyzing it (1)." Simply, an interpretation or decision can be no better than the analytical data on which it is based. Thus, it is essential in environmental studies based on analytical data that the entire project from sampling to interpretation be included in a quality control and assurance program to yield the maximum confidence in the results and decisions.

The parameters to be controlled in an effective environmental analysis study are schematically illustrated in Figure 1. It is based on a solid foundation of planning with validated standard operating procedures and topped with a well-trained analyst. Control of these parameters and the auditing of the results is the basis of an effective analytical quality control and assurance program.

Quality control and assurance programs should be broadly based and it is essential that the three primary participants, the field sampling expert, the laboratory analysts and the planner-interpreter get together early in the planning stages to clearly define the analytical problem and coordinate the sampling and analysis.

Figure 1. Parameters to be controlled in a program of trace analysis of environmental samples.

The first step in planning and developing a standard operating procedure (SOP) is to define the analytical problem and the end use of the data. This should include at least the following:

- elements or compounds to be determined,
- their typical concentration and normal range,
- accuracy, precision and reliability required,
- number of analyses per day and turn around time required,
- sampling frequency and sample size
- physical form.

Each of these parameters will tend to restrict and limit the possible choice in sampling and analytical techniques. This information should then

be combined with information on sampling and analysis capabilities available to develop an optimum procedure which will include everything from sample collection, storage, preparation and analysis. It should also include a sample flow chart in addition to an organizational chart to facilitate logistics and to clearly delineate responsibility particularly when work must be coordinated between more than one laboratory and/or organization.

The primary purpose of this report is to outline the major points to consider in developing an analytical quality assurance program for the analysis of trace concentrations of priority and toxic pollutants in environmental samples. Since the protocol for the collection of environmental samples is highly dependent on the nature and purpose of the specific investigation and program in question, a detailed and informative review of this area is too complex to be covered here, thus only the major points will be presented and discussed. Quality assurance in an analytical laboratory also represents a complex problem, but the required protocol can be formulated in general terms outside the context of any particular analysis or analysis requirement. This latter process is based on

1. The establishment of valid SOPs and
2. quality assurance audits.

The first part of this report will deal with quality control and assurance. The main points required by an effective sampling and storage program will be highlighted in the middle with the major emphasis on laboratory procedures at the end.

QUALITY CONTROL AND ASSURANCE

Quality control (QC) and quality assurance (QA) have come to mean many things and to some, both simply refer to good laboratory technique. Although good laboratory technique is required for both, much more is involved and they have quite different functions (2).

QUALITY in the analytical laboratory is often considered to be synonymous with accuracy. Although this is an important parameter, others such as time per analysis, cost per analysis, precision, meeting milestones and schedules, budgets, etc. are also important characteristics of quality. In the final analysis, the end user is interested in how well

the data meets his needs and expectations. Thus, quality cannot be completely defined until the application of the results is clearly understood.

CONTROL is a management tool through which standards are established and met. It consists of five steps.

1. Setting of quality standards, specifications and criteria,
2. appraising conformance to these standards,
3. acting when the standards are exceeded,
4. planning for improvement in standards, and
5. documentation.

Control implies that the impact on the standards of different variables is understood and that the standards can be maintained with appropriate emphasis on specific variables. The statistical counting error in such analytical procedures as x-ray fluorescence (XRF) and neutron activation analysis (NAA), for example, depends strongly on the counting rate and the length of the counting interval. Thus, the analytical precision can be improved by either counting for a longer period of time or at a higher counting rate so long as it is consistent with the other experimental requirements (3,4,5).

ASSURANCE is anything that inspires confidence.

QUALITY CONTROL consists of a universal series of steps which when applied to problems of analytical quality control can be listed as follows:

1. Selecting the procedural steps and parameters to be regulated
2. choosing the units of measure
3. setting standard values - specifying quality characteristics
4. establishing a quality measuring device
5. conducting actual measurements
6. interpreting the difference between actual and standard values
7. decision making and acting on the differences observed

QUALITY ASSURANCE is the activity of providing to all concerned the evidence needed to establish confidence that the quality function is being performed adequately. It will usually consist of surveillance of the SOP and auditing of the results with blind samples and standards.

Establishing a Quality Control and Assurance Program

The first step in establishing a quality assurance and control program is to obtain a thorough understanding of the end use of the quantitative results and define the quality parameters. The second step is to establish SOPs which include sampling, sample storage, pretreatment and analysis, reagents, standards, supplies, etc. The SOP represents the QC plan and should also include specifications such as replicate reproducibility, calibration procedures, accuracies to be achieved on known standards, etc. The third step is to validate that the SOPs yield results which meet the established quality criteria. During validation, each step is examined for potential sources of error, and the magnitude of each error estimated. Special methods studies should be conducted to determine the possibility of improving the results by reducing the most significant sources of error. It is important to realize that quality cannot be controlled until quality is achieved.

The fourth and last step is the development of a QA plan which yields documented, objective evidence from which confidence in the analytical results can be derived. It should include QA sampling frequency (100%, random, etc.), a quality audit or independent review or check of some aspect of quality performance, presentation of QA data (tabulation, narrative, index, or graphic) and established boundaries and actions. Quality audits should be legitimate, consist of a study of actual practice against some concept of good practice, be carried out by a trained, independent person and be scheduled in advance.

Although QC and QA is everybody's job, the responsibility must be assigned to a single individual who will review the QA data and has the authority to make a decision and take the necessary action (6).

FIELD SAMPLING

The objective in sampling the environment is to obtain a small portion that is representative of the entire body at the instant in time it was sampled. Once the sample is taken, it is essential that the constituents of the sample stay in the same condition as when the sample was collected. Thus, the primary objectives of field sampling are that

- the samples be representative of the system studied and
- the sample's integrity be protected from loss of constituents and contamination.

It is essential that every effort be made to satisfy these two criteria because of the

- unique nature of the sample,
- difficulty and cost required to obtain additional samples,
- extensive and costly analytical and interpretive work to be done on the sample, and
- the significance of the conclusions to be derived from the study.

The details of collection vary so much with type of sample and local conditions that no specific recommendations would be universally applicable. Some of the main parameters to consider, however, are discussed.

The first requirement is that a statistically representative sample be obtained which represents the average composition of the mountain, river, plant, animal or organ studied. This requires establishing the number of samples required, the frequency and duration of sampling, the time and location of sampling, etc. Should a few random samples be taken or should a large number of samples be collected on the basis of a sampling pattern laid out according to a statistically derived plan? Should the samples be analyzed individually or should they be composited? What flow rates and volumes should be sampled and what sampling implements should be used. These are but a few of the questions that must be answered and the answers evaluated relative to how well they meet the analytical and quality objectives (7,8,9).

An integral part of any field sampling program should be a quality control audit conducted by an independent person under as nearly as possible identical conditions without affecting the normal sampling routine and at random times without the knowledge of those conducting the normal sampling program. This could consist of complete duplication of the entire sampling and analysis program (100% audit) but would not be practical with most programs. At a minimum it should consist of going out to field sampling stations and checking such things as flow rates, dates, times, sample identification, sampler identifications, locations, and other parameters which can be easily checked without significantly disturbing the samples

being collected. Random field replicates should also be collected where possible. This type of field sampling program should encompass between 5 and 10% of the samples at a minimum.

SAMPLE PRESERVATION

The primary concern in sample handling and storage is maintaining the integrity of the sample; i.e., prevent the loss of constituents and/or contamination. Maienthal and Becker (10) have recently reviewed storage methods for trace elements and have concluded that even though there is an abundance of reports, many of them are contradictory and that much of the published analytical data is apparently inaccurate because of such problems as gross sampling contamination or subsequent procedural contamination and failure to make proper blank corrections. They also concluded that there exists the necessary expertise, techniques and materials to provide viable long-term stored samples for most trace elements in most matrices; but few are using these techniques because of the expense.

The method of preservation will depend strongly on the type of material stored and the chemical components to be determined. Dry geological samples require much less concern than water or biological material. Irregardless of the sample type of storage method used, a clearly defined standard operating procedure for storage is required. This should include method of sample identification, chain of custody, container type and cleaning method, holding time, preservative and preservation method used in addition to listing the field and laboratory data that should be recorded (11,12,13).

The first consideration is the choice of the container. For inorganic compounds, containers made from FEP Teflon are the first choice with high purity quartz next. Conventional polyethylene or TFE Teflon are also adequate for most applications. All cleaning and sample treatment should be done in laminar flow hoods or a clean room. Cleaned plastic gloves should also be worn in all phases of cleaning, sampling, etc. (11,12,13). For ultra-trace analysis, Patterson has suggested a rather elaborate HNO_3 washing procedure (14) while others have found that a three-day leach in 8 to 16 M HNO_3 and rinsing with high purity water adequate for most routine analyses (12, 13).

For organic analysis glass seems to be the best suited material for sampling and sample storage. Pre-cleaning of the containers and all parts

of the sampling train prior to sampling is essential if contamination is to be avoided. This pre-cleaning should consist of at least the normal washing with detergent followed by thorough rinsing with blank water and methylene chloride and baking in a muffle furnace at 450°C for four hours (baking for longer periods or at higher temperatures may distort glassware). Dichromate and sulfuric rinses would also be desirable prior to baking. Cleaned glassware should be stored in a cleanroom in which the air has been filtered through carbon⁽¹⁵⁾ and stored no longer than two weeks prior to use.

Collection of samples for organic analysis should be immediately followed by cooling to about 0°C and removal from light. In the analysis of water for organics, care should be taken to minimize void space in the containers.

One of the surest ways to prevent loss of trace inorganic pollutants is to analyze the entire sample plus the container. This has been done by collecting the sample in double lined polyethylene bags and immediately freezing the sample. The sample is then freeze dried and the residue and the containing bag analyzed by instrumental neutron activation analysis. This assures minimum sample handling and the only element potentially lost is mercury. Water can also generally be stored for trace metals by acidifying to a pH of 2 or less with NH_4OH .

LABORATORY ANALYSIS

The decisions made on the basis of analytical data can be far-reaching indeed. It can help to convict a man of a crime in forensic investigations, it can dictate the medical treatment in clinical analysis, it can determine the fate of an industrial process, establish a violation of pollution standards requiring action on the part of the pollution control authorities or result in incorrect conclusions and future plans in environmental investigations. With the present emphasis on legal action, the analyst should be aware of his responsibility to provide laboratory results that are a reliable description of the sample. Furthermore, the analyst must be aware that his professional competence, the procedures he has used, and the reported values may be used and challenged in court. To satisfactorily meet this challenge, the laboratory data must be backed up by an adequate program to DOCUMENT the proper control and application of all of the factors which affect the final result and their accuracy.

Since it can always be assumed that the accuracy and validity of the analytical results will be questioned, the analyst must develop and maintain a healthy skepticism of his results and build into his procedures adequate controls and cross checks. If this skepticism develops, quality control and assurance becomes an important and integral part of the normal operation of the analytical laboratory.

There are two principal steps in developing confidence in a laboratory's analytical accuracy. These are

- establishing validated standard operating procedures with built in controls and internal cross checks and
- developing an approved standard operating procedure for quality assurance consisting of audits to assure that the analytical standard operating procedure is followed and to document the procedure's accuracy.

Quality control in the analytical laboratory consists of a plan or SOP which is designed to provide analytical results that are adequate to meet the needs of the end user. Inherent in this is the assumption that the procedure has been verified as being valid for unless an analytical process is under such control that the results are reproducible, it is not a proper object of routine quality control, i.e., unless quality has been achieved, it is not controllable or measureable.

Each step of an analytical process must be demonstrated to be valid, i.e. a test tube must be shown to be free from Zn contamination before it can be used for trace Zn analysis. Calibrations should be built into the SOP where ever possible and documented. Fresh standard solutions should be compared with old. Instrumental responses to calibrators should be recorded. Results from the analysis of known samples should be noted and linearity and recovery check results documented.

Whereas quality control establishes the analytical quality, quality assurance is the surveillance and documentation that the quality is being maintained. Quality assurance in the analytical laboratory is based on the analysis of blind replicate specimens and/or standards. These are listed in Table 1 along with the type of information they provide. They are also schematically illustrated in Figure 2. All provide information on precision. Recycled secondary standards and spike recovery specimens provide

Table 1

TYPES OF QUALITY ASSURANCE SPECIMENS AND THE INFORMATION THEY PROVIDE

<u>Specimen Type</u>	<u>Information Provided</u>
Recycled Specimen	Precision
Recycled Secondary Standard	Precision, Indication of Accuracy
Spike Recovery Specimens	Precision, Indication of Accuracy
Intermethod Comparisons	Precision, Estimate of Accuracy
Interlaboratory Comparisons	Precision, Estimate of Accuracy
Recycled Certified Standard	Precision, Measurement of Accuracy

an indication of the accuracy. Intermethod and interlaboratory comparisons can provide a very good estimate of the accuracy while the analysis of blind, recycled, certified standards yields an excellent estimate of the accuracy, particularly when the certified standard is of the same general composition as the specimens.

Recycled specimens should be submitted under a false identification code, as should all quality assurance samples so as to avoid prejudicing the analyst. Analysis of recycled specimens will have an additional source of error due to sample inhomogeneity. Thus, if the procedural error is to be adequately checked, only the most homogeneous samples should be used for this purpose. Analysis of spiked specimens should be done at several different concentrations so as to minimize potential errors due to nonlinearity of response and/or interferences. There is an additional source of potential error which is due to differences in the chemical or physical form between the spike and the original analyte in the specimen. Intermethod and interlaboratory comparisons are most effective when they involve totally independent analysis methods which are based on different phenomenon such as atomic absorption, x-ray fluorescence and neutron activation analysis or high performance liquid chromatography, gas chromatography, mass spectrometry or a wet chemical colorimetric method for organic pollutants. Flame emission and flame absorption would not be considered independent methods nor would gas chromatography using two different columns because both measurements rely on the same phenomenon. It is also desirable in comparisons between laboratories that different standards be used.

Figure 2. Schematic illustration of the six methods used to establish the analytical precision and accuracy of a method.

Understanding and knowledge of the system being studied can also be used to build in additional assurance through correlation studies. In water analysis, for example, chemical oxygen demand and total organic carbon are often highly correlated as well as total dissolved solids and conductivity, total suspended solids and turbidity, and hardness and calcium and magnesium content.

PROPOSED QUALITY ASSURANCE PROGRAM

Background

The Imperial Valley Environmental Project (IVEP) was initiated to establish an environmental data baseline for the Imperial Valley and to assess the potential environmental impact of future geothermal installations in the valley. The project involves the taking and analysis of a large number of environmental samples to assess the air, water and ecosystem baseline concentrations of specific elements related to geothermal energy production. These samples include air particulates deposited on filters, water, biological, vegetative and geological samples. The samples have already been collected, stored and are in the process of being analyzed by both internal and outside contract laboratories.

Recommendations

Since the samples associated with this study have already been collected and are in the process of being analyzed, this section will consider only the laboratory QA as applied to the specific problems of Lawrence Livermore Laboratories geothermal baseline study.

1. Written standard operating procedures should be obtained for all sampling, storage and analysis procedures regardless of whether the event has already passed or whether it is associated with an outside contract or internal laboratory. If the event has already occurred, it will provide needed documentation required for long-term assessment of the data's quality.
2. A laboratory QA program should be developed that incorporates appropriate parts of the six primary QA audit samples, recycled specimens, secondary standards, spiked specimens, certified standards, interlaboratory and intermethod comparisons. For example, all six might be appropriate for water samples while only three or four might be conveniently applied to vegetative material. The QA program should also have a description of how the QA data is to be displayed, boundary conditions to maintain and what action should be taken when these boundaries are exceeded.

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