QUALITY ASSURANCE PROGRAM FOR THE ANALYSES OF CHEMICAL CONSTITUENTS IN ENVIRONMENTAL SAMPLES*

The following program of quality assurance is for use by laboratories engaged in the analysis of organic and inorganic chemicals, metals, and general analysis parameters in environmental samples.

Each laboratory is responsible for maintaining a continuing record of the data from all quality control checks and for using these data to make decisions on the acceptability of the analytical results as they are acquired. All quality control data generated, problems identified, and corrective actions taken to resolve the problems are to be recorded and provided to the responsible authority when reporting the analytical results. As available, quality control (QC) check samples of known value and performance evaluation (PE) samples should be analyzed by the laboratory prior to initiation of the analytical program.

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A. Intralaboratory Quality Control

As a part of its intralaboratory analytical quality control program, the laboratory must develop single laboratory precision and accuracy criteria for each parameter that it is required to measure. These criteria must compare favorably with published data. Initially, these data may be applied over a broad concentration range. As more data accumulate, the precision and accuracy of the method should be updated and criteria developed for multiple narrower ranges.

1. Precision - To determine the precision of the method, a regular program of analyses of replicate aliquots of environmental samples must be carried out. The precision criterion should be developed from 15 sets of replicate results accumulated over a period of time during the routine analysis program. At least two replicate aliquots of a well mixed sample must be analyzed with each set of 20 samples or less analyzed at a given time. These replicate data must be obtained for each parameter of interest.

Initially, samples selected for replicate analyses should be those that are most representative of the interference potential of the sample type. For example, in the current Effluent Guidelines Verification Program, the influent to the treatment process would be appropriate. As the program progresses, samples representing the entire range of concentrations and interference potential should be designed into the replicate analyses program.

After 15 replicate results have been obtained, calculate the range (R_i) of these results as follows:

$$R_i = \left| X_{i1} - X_{i2} \right|$$

where R_i is the difference between the results of the pair (X_{i1} and X_{i2}) from sample i=1 through n. The concentration of each sample is represented by the mean:

$$\overline{X}_i = \frac{(X_{i1} + X_{i2})}{2}$$

where $\overline{X}_i$ is the average of the results of the replicate pair. A preliminary estimate of the critical difference (R_c) between replicate analyses for any specific concentration level (C) can be calculated as:

$$R_c = 3.27\ (C \sum_{i=1}^{n} R_i)/(\sum_{i=1}^{n} \overline{X}_i).$$

From these data develop a table of such R_c values for various C values that span the concentration range of interest.

These preliminary critical difference values may be used to judge the acceptability of the succeeding replicate results. To do this, calculate the mean ($\overline{X}$) and difference (R) between the replicate results. Referring to the table of critical range values developed above, find the C nearest to $\overline{X}$ and use its R_c to evaluate the acceptability of R. If the R is greater than R_c, the system precision is out of control and the source of this unusual variability should be identified and resolved before continuing with routine analyses. Record the results of all replicate analyses and periodically (after 25 to 30 additional pairs of replicate results are obtained) revise, update, and improve the table of critical range values.

2. Accuracy - In addition to the initial determination of the precision of the method, a program must be maintained to verify that the laboratory accuracy continues under control. This program is concurrent to the spiked

sample analysis program outlined below and is carried out by preparing check standards and analyzing them according to the method. The check standards should be approximately equal to the concentration found in routine samples. Alternately, one standard above and one standard below the midpoint of the range of the method should be used. Analyze the standard and calculate O_i (the observed value). The percent recovery (P_i) is then calculated as follows:

$$P_i = \frac{100\ (O_i)}{T_i}$$

where T_i = the true value.

After determining the P_i for approximately 15 check standards, calculate the mean ($\bar{P}$) and standard deviation (S_p) of the percentages as follows:

$$\bar{P} = \frac{\sum_{i=1}^{n} P_i}{n}$$

and:

$$S_p = \sqrt{\frac{1}{n-1}\left[\sum_{i=1}^{n} P_i^2 - \left(\sum_{i=1}^{n} P\right)^2/n\right]}$$

where n = the number of results available.

If the percent recovery for succeeding check standards is not within the interval of $\overline{P} \pm 2\ S_p$, the system should be checked for problems. If problems exist, they must be resolved before continuing with routine analysis. This criteria is tighter than the generally accepted $\overline{P} \pm 3\ S_p$ but will result in more accurate data for real samples if these check standards are used to adjust the calibration curve.

At least one check standard must be analyzed along with each set of 20 samples or less that is analyzed at a given time. This check standard data must be obtained for each parameter of interest.

Record the recovery of all check standards and periodically revise, update and improve the accuracy criteria.

3. Recovery - Determine the recovery of the method for the analysis of environmental samples by adding a spike (T_i, true value) sufficient to approximately double the background concentration level ($\overline{X}_i$) of the sample selected earlier for replicate analysis (Section A1). If the original concentration is higher than the midpoint of the standard curve (range of the method), then the concentration of the spike should be approximately one-half the original concentration. If the concentration of the

original sample was not detectable, the concentration of the spike should be five to fifteen times the lower limit of detection. The volume of standard added in aqueous solution should not dilute the sample by more than ten percent. The volume of standard added in an organic solvent solution should be kept small (100 µl/l or less), so that the solubility of the standard in the water will not be affected.

Analyze the sample, calculate the observed value (O_i), and then calculate the recovery for the spike as follows:

$$P_i = 100(O_i - \overline{X}_i)/T_i$$

where P_i is the percent recovery. If the sample was diluted due to the addition of the spike, adjust $\overline{X}_i$ accordingly.

After determining P_i for at least 15 spike results, calculate the mean percent recovery ($\overline{P}$) and standard deviation (S_p) of the recovery as follows:

$$\overline{P} = \left(\sum_{i=1}^{n} P_i\right)/n$$

$$S_p = \sqrt{\frac{1}{n-1}\left[\sum_{i-1}^{n} P_i^2 - \left(\sum_{i=2}^{n} P_i\right)^2/n\right]}$$

where n = the number of percent recovery values available.

If the percent recovery of the spike is not within the interval of $\overline{P} \pm 3\ S_p$, the system accuracy is out of control and the source of this systematic error should be identified and resolved before continuing with routine analysis.

At least one spiked sample must be analyzed along with each set of 20 samples or less that is analyzed at a given time. This spiked data must be obtained for each parameter of interest. Record the recovery data of all spiked analyses and periodically (every 25 to 30 data points) revise, update, and improve the accuracy criteria.

B. Additional Routine Quality Control Practices

In addition to the foregoing formal quality control program, certain other practices must be included during routine analyses by the laboratory to eliminate determinate errors and to insure the quality of the data. These practices include: instrument calibration and performance checks, preparation and daily check of calibration curves, method blank analyses, and field blank analyses. Some of these operations are common to all analytical methods and some are unique to specific methods.

For additional information and guidance in analytical quality control practices refer to the U. S. Environmental Protection Agency's "Analytical Quality Control Handbook" (1).

1. Operations Common to all Methods

   a. Standard Curve - Prior to the analysis of samples, a standard curve that covers the entire working range of the method must be constructed with at least five standards, including one near the upper limit of the concentration range and one near the lower limit of the concentration range. The other standards should be equally spaced throughout the operating concentration range.

      Each day, if operation is continuous, or prior to analyzing each group of samples, if operation is non-continuous, analyze a minimum of two standards to establish the validity of the original standard curve. These standards should represent the range of the standard curve, i.e., one above and one below the midpoint of the standard curve. If these standards fall outside the established limits, a new standard curve must be constructed. These limits

should be established by the analyst as a part of his ongoing quality control program.

b. Method Blank - A method blank must be determined for each set of samples analyzed and whenever a new source (new container) of reagent or solvent is introduced into the analytical scheme. (NOTE: the individual solvents and reagents should be checked for purity prior to use in determining the method blank or in the analysis of samples.)

To determine the method blank, take a quantity of reagents equivalent to that used in the analysis of the sample and carry them through the entire analytical procedure including all glassware and other materials that come into contact with the sample. Determine a method blank for each class of compounds to be determined, i.e., pesticides, base-neutrals and acids, metals, phenolics, cyanides, etc.

Reagents having background levels that interfere with the compounds to be determined must be purified and shown to be acceptable or replaced with some that

are acceptable prior to proceeding with the analyses. Problems encountered and corrective actions taken should be reported to the responsible authority for information and possible resolution of problems encountered by other analysts.

c. Field Blanks - A field blank must be analyzed with each set of samples from a given source. This is particularly important whenever automatic samplers are used for collection of samples as in the current Effluent Guidelines Program. The blanks must be analyzed in the same manner as the sample. Preparation of field blanks is described in the sampling and analysis protocol (2). Field blanks for purgeables are sent from the laboratory to the sampling site and returned as a check on possible contamination of the sample by permeation of volatiles through the septum seal.

When interferences occur, the analytical results must be discarded unless sufficient data from these blanks is available to permit correction of the results.

2. Operations Specific to Organic Analysis by Gas Chromatography-Mass Spectroscopy (GC-MS)

a. Calibration Check for the GC-MS System - At the beginning of each day's operation, test the calibration, resolution, and sensitivity of the GC-MS system as follows:

When analyzing for purgeable organics or semivolatile acids, check the system by directly injecting and analyzing 100 nanograms of pentafluorobromobenzene (PFBB)[1]. Determine system performance using the ion abundance criteria for this compound listed in Table 1 (3). If this test shows that the system is not properly calibrated retune and recalibrate to meet specifications.

When determining semivolatile base-neutral organics, check by injecting and analyzing 20 nanograms of decafluorotriphenylphosphine (DFTPP)[2]. Determine the system performance using the ion abundance criteria listed in Table 2 (4). If this test shows that

[1]Available from Aldrich

[2]Available from PCR, Inc.

the system is not properly calibrated, retune and recalibrate to meet specifications.

b. Internal Standards - The use of internal standards provides a convenient mechanism for checking the total analytical procedure. Their use is recommended when appropriate standards are available. The internal standards should be selected by the analyst based upon prior knowledge of the sample source and type. They should be similar to the compounds being determined, but not co-elute with them. At least two internal standards should be selected for each class of compounds of interest, e.g., purgeables, pesticides, base-neutrals, and acids, so that the retention time range of the analysis is covered. Having selected the appropriate internal standards, spike an aliquot of every sample at the appropriate time, i.e., just prior to purging the volatiles or just prior to extraction of pesticides, base-neutrals, and the acids. If available, deuterated compounds are recommended for use when analyzing by GC-MS.

c. Quantification by GC-MS - Using a GC-MS system, e.g., Finnigan 1015 series or equivalent, prepare a multi-point calibration curve for each compound that is to be measured. This curve should be sufficiently accurate to permit a rough estimate of the concentration of the unknown for several weeks. From this estimate, make up a single concentration of standard for the compound or compounds of interest and analyze on the same day as soon as possible after the sample is analyzed. The concentration of this standard should be within a factor of two of the actual concentration of the unknown and is used to calculate an accurate estimate of the concentration of the unknown.

Peak areas should be integrated using ion abundances from two or more of the characteristic ions

for the priority pollutants. The GC-MS system must have a program capable of supporting this type of integration.

(1) PROCEDURE

(a) Prepare a minimum of three standard solutions (10 ng/µl, 100 ng/µl, and 500 ng/µl concentrations are suggested) of each of the compounds that are to be measured. One or more compounds may be present in the same standard solution. Record the total ion current profiles for each of the solutions, and integrate the peak areas of the target compounds over two or more of the selected characteristic ion abundances. Prepare a separate plot of concentration versus peak area for each ion and each compound.

(b) As described earlier under B. 2. a, the stability of the GC-MS total system must be verified daily with the use of standard reference materials, i.e., decafluorotriphenylphosphine, pentafluorobromobenzene, and other standards and calibration diagnostic programs. Whenever

significant instability is observed, i.e., any random peak area change greater than 25% or any drift sufficient to require recalibration of the mass scale, step (a) must be repeated.

(c) Measure the total ion current profiles of the unknowns. Integrate the peak areas of the target compounds over the characteristic ion abundances. Using the calibration curves, make a rough estimate of the concentration of each of the unknowns using the appropriate peak areas.

(d) Prepare a standard solution for each compound to be measured that day. The concentration should be as close as possible to the concentration of the unknown and always within at least a factor of two. More than one compound may be in this standard solution. Measure the total ion current profiles of the standards. Perform peak area integrations with the unknowns and standards using two of the characteristic ions. Calculate the

unknown concentration by interpolation of peak areas and the known concentration of the standard. If the results are similar for the two ions, report the average concentration. If the results differ by more than 50%, select another ion or ions until two are found that give similar results.

(e) For 10% of the samples, duplicate the measurements of the unknowns and standards and report both the unknown concentration measurements.

(f) The data shown in Table 3 were obtained by a single laboratory using the above procedure with a series of blind spikes in water. The average bias from the spiked value was-30%.

C. Interlaboratory Quality Control

In addition to establishing the precision and accuracy of the method and routinely analyzing replicate and spiked samples, the laboratory must also analyze a quality control (QC) check sample, at least twice annually, and a performance evaluation (PE) sample, at least once annually, for parameters of interest as they are available from the

Quality Assurance Branch, EMSL, Cincinnati. This is in addition to the initial checks made before sample analyses begin. These quality assurance samples will be forwarded to the laboratory at the request of the responsible authority. Samples currently available from EMSL - Cincinnati include: pesticides, polychlorinated biphenyls (PCBs), purgeable organics, metals, minerals, nutrients, and the demand series. The results of the QC check sample should be recorded and forwarded to the responsible authority. The results of the PE samples should be recorded and forwarded to EMSL, Cincinnati, Quality Assurance Branch.

TABLE 1

PFBB Key Ions

Ion Abundance Criteria

Mass	Ion Abundance Criteria
78	less than 1% of base peak
79	15-35% of base peak
80	4-8% of mass 79
116	less than 1% of base peak
117	base peak
118	4-8% of mass 117
166	less than 1% of base peak
167	65-85% of base peak
168	5-9% of mass 167
245	less than 1% of base peak
246	75-98% of base peak
247	5-9% of mass 246
248	75-98% of base peak
249	5-0% of mass 248

Mass 248 must be 93-99% of mass 246

TABLE 2

DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40-60% of mass 198
197	less than 1% of mass 198
198	base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	1% of mass 198
441	less than mass 443
442	greater than 40% of mass 198
443	17-23% of mass 442

TABLE 3

Example of Quantitative Data Obtained With GC-MS by a Single Laboratory Using a Single External Standard

Semivolatile Organics	Reported Value µg/liter	True Value µg/liter	% Deviation
Solvent Extract Sample 1			
trichlorobenzene	0.3	0.79	-62
n-octadecane	1.4	2.17	-35
pentachlorophenol	0.5	0.75	-33
fluoranthene	1.5	2.97	-49
di-(2-ethylhexyl)phthalate	1.3	1.42	- 9
Solvent Extract Sample 2			
trichlorobenzene	0.5	0.79	-37
n-octadecane	0.6	0.87	-31
pentachlorophenol	1.5	1.76	-15
fluoranthene	0.5	0.71	-30
di-(2-ethylhexyl)phthalate	2.5	3.57	-30
Solvent Extract Sample 3			
trichlorobenzene	0.6	0.79	-24
n-octadecane	2.2	3.25	-32
pentachlorophenol	6.2	3.77	+64
fluoranthene	1.4	2.38	-41
di-(2-ethylhexyl)phthalate	0.8	0.71	+13
Volatile Organics Sample 1			
Chloroform	6.3	10.7	-41
1,2-dichloroethane	1.3	1.05	+24
carbon tetrachloride	~1	1.86	-46
dichlorobromomethane	0.6	0.81	-26
dibromochloromethane	0.7	1.03	-32
bromoform	2.3	4.81	-52
Volatile Organics Sample 2			
Chloroform	69.2	74.6	- 7
1,2-dichloroethane	3.4	3.06	+11
carbon tetrachloride	~5	3.87	+29
dichlorobromomethane	10.1	9.15	+10
dibromochloromethane	6.4	7.12	-10
bromoform	7.2	9.23	-22

References

1. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", June, 1972. Available from U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268. New edition in press, to be available Fall, 1978.

2. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants", U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, April, 1977.

3. Budde, W. L., and Eichelberger, J. W., U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268.

4. Eichelberger, J. W., Harris, L. E., and Budde, W. L., Anal. Chem. 47, 995 (1975).