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QUALITY CONTROL ASSURANCE PROGRAM for PRIMARY **IN-STREAM** MONITOR **NETWORK** 



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Quality Control Assurance Program

for

Primary In-stream Monitor Network

April, 1977



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# INTRODUCTION

# ORSANCO Quality Control Assurance Program for Primary In-stream Monitoring Network

The following procedures outline a program for quality control assurance for the ORSANCO regional river monitoring program. Essentially, the procedures are in conformance with what has been previously published in the Federal Register as proposed guidelines for monitoring (Appendix A, Section 106 and the forthcoming guideline to regions and states under the so-called Model States Program). Elements of the program are: 1) representative sampling; 2) sampling devices and preservation of samples; 3) shipment of samples; 4) chain of custody; 5) analytical procedures; 6) quality control of data and; 7) data reporting.

# 1) Representative Sampling

Initially, each sampling point will be selected by making measurements with field instruments for temperature, pH, conductivity and dissolved oxygen at various points and depths across the river, following the procedures suggested by the USGS. With the information obtained from the initial survey, representative points will be chosen. This multipoint examination will be performed periodically to insure continued validity of the selected point.

# 2) Sampling Devices and Preservation of Samples

The conventional "Ohio River" sampler, sometimes called the Sargent sampler, will be used for sample collection. This sampler has a volume of about 3 - 4 liters and can accommodate two DO bottles when such samples are required. The sampler is made of cast aluminum with stainless steel fittings and weighted from the outside so that it may be used for metals sampling.

A set of bottles, either of plastic or glass, sterile or non-sterile as required, and of appropriate volume will be supplied for each sampling location. Sample bottles will be spiked with the appropriate preservative by laboratory personnel before the bottles are sent into the field, or by the sample collection at the time of collection using pre-packaged ampules of preservative. Reagents used for preservatives are checked for acceptable quality and freedom from contamination by a quality control officer. Methods of preservation for all samples will adhere to guidelines suggested in the <u>EPA Manual of Methods for the Chemical</u>

\*The quality control assurance program was developed in cooperation with Robert Kroner, consultant. Analysis of Waters and Wastes, 1974. All samples requiring preservation will be iced (4°C) and air shipped (to insure delivery within 24 hours) the same day collected, after being placed in styrofoam coolers sent to the analytical laboratory. All samples requiring field filtration (ie. trace metals) are filtered immediately after collection in the field through a membrane filter (0.45). In cases where recommended holding times cannot be met, the laboratory quality control officer will determine whether samples are to be analyzed or discarded.

# 3) Shipment of Samples

Shipping containers will be small styrofoam coolers with impact resistant outer coverings and snap-fitted lids to maintain cooling efficiency. Ice needed for cooling will be obtained locally. The small styrofoam coolers will be packaged along with other similar containers in a larger fiber shipping carton for convenience in handling and shipping.

A standardized protocol for shipping the sample cartons to the laboratory in minimum time will be established.

Measurements which can be performed efficiently and accurately in the field will be performed at the time of collection to reduce the number of shipping containers required. For such measurements, field instruments will be calibrated by approved techniques as specified by the manufacturer on each day of use. Such calibration data will be permanently recorded in field notebooks. (Section II)

Arrangements will be made with local laboratories to perform those measurements requiring minimal holding times, ie., coliform, 5-day BOD.

# 4) Chain of Custody

The sample collector and his assistant(s) will record all information pertinent to the sample on sample bottles, using waterproof ink and again in an approved log form. The sample collector will attest by signature on the bottle and in the log form to the validity of the sample.

All samples having been duly recorded, will be delivered by the sample collector to the authorized carrier for shipment to the receiving laboratory. At the receiving laboratory, all samples will be delivered to the authorized laboratory personnel.

In special cases such as enforcement cases where it is legally imperative that sample integrity be maintained, special chain of custody procedures will be followed as required to satisfy the parties involved.

# 5) Analytical Procedures

Analytical methods used for analysis of all samples will conform

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to those methods cited in Federal Register, Vol. 38, No. 199, Part II, Guidelines for Establishing Test Procedures for Analysis of Pollutants.

In the event that an analytical variance is required, the request for the variance will be made by the ORSANCO Executive Director following the protocol prescribed in the Federal Register cited above.

The choice of methods for certain biological and microbiological examinations for which no official guidelines have been promulgated, will be made following advice from qualified authorities.

# 6) Quality Control of Data

Quality control of analytical data will be achieved by: a) routine calibration and maintenance of laboratory instruments and equipment; b) routine verification of working standard curves; c) determination of individual method precision and accuracy; d) use of reference samples and blind samples to verify daily results, e) use of reference samples and standards, as knowns or unknowns as additional checks. (See Section IV)

# 7) Reporting of Data

All data will be reported using the accepted reporting levels (see Section III) and in a form suitable for computerized storage and retrieval. Sample data along with the quality control data will be sent by the analytical laboratory to the ORSANCO office for review before computer entry and before samples are discarded. For storage and retrieval of data, the most recently distributed STORET parameter codes will be used. (See Section III)

Samples will not be held longer than seven days after the data has been reported to ORSANCO, except for those samples involving chainof-custody and enforcement actions.

# Calibration and Quality Control of Data for Automatic Monitors

In general, the calibration of the instrument will be performed according to the manufacturer\*s recommendations by a duly qualified representative of the manufacturer or Commission representative,(See Appendix 5 for a detailed description of procedures.) All instruments will be inspected, repaired as necessary, calibrated and restandardized on a fixed schedule of seven to ten days.

The procedures to be used will be as follows:

pH - clean electrodes as necessary, calibrate using standard buffers at 4 and 7 to insure linearity. When practical, a separate pH check may be run with a pre-calibrated field meter against a stream sample.

Temperature - clean sensor, calibrate with a standard NBS certified thermometer.

Dissolved oxygen - clean sensor, standardize against a DO measurement using the Winkler method. When practical, a separate check may be made against an air-calibrated sensor.

Conductivity - calibrate with standard conductivity solutions at or near stream conductivity and at  $\pm$  100 micromhos. When practical, a check may be made against an actual stream sample using a pre-calibrated field meter.

Chloride - calibrate at three points, bracketing the stream reading using standard chloride solutions. When practical, a check may be made against an actual sample, using a manual titration.

A record of maintenance for each monitor will be kept on a permanent record book showing the date of maintenance and standardization with readings before and after calibration. Accumulated data will be discarded (or flagged) if the maintenance update shows sensor drift of  $\pm$  5% from the true reading.

Specific instructions to the field personnel concerning safety, sample collection, preservation and shipment techniques and the use and protection of field equipment are contained in "Quality Control in Field Sampling and Analysis". (Section II)

#### River Cross Section

For

# ORSANCO Monitoring Program

The ORSANCO River cross sectioning program is conducted to provide the following specific objectives at all of the monitoring stations covered by the moni-toring strategy:

- 1. To determine the variation in dissolved oxygen, pH, conductivity and temperature in the river at each station.
- 2. To determine the adequacy of the robot and manual sampling locations, if they are representative of the dissolved oxygen, pH, temeprature and conductivity of the river.
- 3. To compare the robot data with the observed river values at the time of cross sectioning.

# Procedure

The cross sectioning of each of the 37 stations consists of performing pH, temperature, dissolved oxygen and conductivity measurements at three or more points across the river, depending upon the width of the river and other hydrologic factors. The depth measurements are made at five foot intervals starting about two feet from the bottom and ending at one and a half feet from the surface.

Measurements are made at each specific manual and automatic sampling point at at the same location.

Measurements are also made on the water samples from intake lines to the robot monitor, to determine if there are any changes in water quality, especially the dissolved oxygen concentration as the water flows through the intake line.

Water quality monitors manufactured by Martek (Model Mark III) and NERA (Model 4) have been used for the river measurements. Accuracy specifications for the instruments are as follows:

Martek III Monitor:

Depth probe =  $\pm$  1.0 percent Temperature =  $\pm$  0.1°C from -2°C to 45°C D0 probe =  $\pm$  0.1 ppm Conductivity probe =  $\pm$  2 percent ph probe =  $\pm$  0.05 pH units NERA Water Quality Monitor:

pH probe =  $\pm$  0.2 pH units D0 probe =  $\pm$  0.1 to 0.2 mg/1 Temperature probe =  $\pm$  0.1° C Conductivity probe =  $\pm$  0.2 percent

All meters are reported by the manufacturers to have an accuracy of approximately  $\pm$  1.0 percent.

Robot monitors and the instruments are calibrated before cross sectioning and the DO probes are checked against Winkler titration.

# Data Analysis

The cross sectional data is analyzed in the following to find the variation of DO, pH, conductivity and temperature within the river and to compare the robot data with the observed values in the river:

1. Plotting cross sectional profile

- 2. Statistical analysis
- 1. Cross sectional profile

Two dimensional charts are prepared which represent the cross section of the river at all stations along the Ohio River and lower reaches of major tributaries. The profiles show the difference between the actual observed values and the overall average for DO, pH, conductivity and temperature.

2. Statistical analysis

A. Discrepancies across the river

The coefficient of variation, or relative variation, is calculated in the following manner to determine the actual variation of DO, pH, conductivity and temperature in the river at all stations, because it is a measure of the dispersion of the average value of these parameters across the river:

$$CV = \frac{SD}{M} \times 100$$

where:

CV = coefficient of variation SD = standard deviation

M = average value of a parameter

The CV value is a relative value which can be used for the purpose of comparing parameters.

B. Adequacy of the robot and manual sampling locations

At the point where each manual sample is collected and at the intake for each electronic monitor, the mean of the samples collected at that vertical section is compared with the range revealed by the ninety-five percent confidence interval.

Ninety-five percent confidence intervals were calculated as:

$$C I_{95} = M_R + 1.96 \sigma_R$$

where:

- M R = overall averages of a parameter in the river
- 1.96 = confidence factor for 5 percent
   level of significance
  - $\overline{V}_{R}$  = standard deviation of a parameter in the river
- C. Comparison of robot data and observed river value

The ninety-five percent confidence intervals calculated above were used to determine if the robot data is within these limits or not.



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# Quality Control in Field Sampling and Field Analysis

This section of the ORSANCO Quality Control Assurance Program for the Primary In-stream Monitoring Network is divided into six units. Each unit is addressed separately to the following aspects of field sampling and analysis:

- 1. Safety in the Field
- 2. Sampling, Sample Handling and Preservation
- 3. Sample Shipment
- 4. Analysis Techniques with Field Instruments
- 5. Maintenance of Monitoring Equipment
- 6. Special Samples

# 1. Safety in the Field

There are a number of situations that each Surveillance Specialist will encounter at different locations, and each of these situations must be given full consideration and attention. At any sampling site, safety is a prime consideration and is discussed at the beginning of this section to emphasize its importance. There is no short cut to safety and no water sample is worth the life of a field man.

If the sampling operation is conducted from a bridge and the vehicle must be parked either on the bridge or at the bridge approach, every reasonable precaution must be taken to minimize traffic hazards. Park the vehicle in the least hazardous place with safety flashers operating. Set out warning cones or warning flags as appropriate. Take the sample as quickly as possible and perform the necessary operations as promptly as possible. Do not linger in the area. Be especially cautious in bad weather and during early morning or twilight hours. If special or unusual conditions exist that the supervisor-in-charge does not know about, report them.

If the sampling operation is conducted from a restricted area (power plant, dam, etc.) check in as appropriate. Do not assume that the guard knows that you are in the area. Register upon entering premises. If hard hats or life jackets are required, use them. Operate your vehicle with special care on the company grounds and park it where it will not be an inconvenience to company personnel or violate company rules.

Since many of the monitors are installed in remote, isolated areas of power plants and water treatment plants, it is a good practice to let local personnel know that you are in the area and should return within a specified period of time. Similarly, let the same persons know when you are leaving the area. By all means, police the area carefully after you have serviced the automatic monitor and have completed the required field analyses. If you observe any unsafe conditions such as electrical hazards, greasy catwalks, etc., report them to the local man in charge.

# 2. Sampling, Sample Handling and Preservation

The ORSANCO Monitoring Network consists of 37 stations, of which 22 are located on the Ohio River and 15 on lower reaches of the major tributaries. This network represents a nucleus of key locations above and below major population centers and industrial areas, and in critical sections of the relatively new higher level pools on the Ohio River. The stations were selected by the Monitoring Strategy Study Team from a compendium of potential sites recommended by the participating agencies for satisfying their need with regard to statutory requirements.

The analytical parameters selected and the frequency of sample (Table1) are designed to provide sufficient information on which to appraise water quality conditions at each location, and to provide for comparisons of quality with other sections of the river. Data reviews in the future may indicate that frequency of sampling be altered, that sampling sites be moved, that additional analyses be added to the existing list, or that some analyses be omitted. Meanwhile, it is the basic function of the Surveillance Specialist to visit the sampling station at the scheduled time and secure the samples in the prescribed manner.

#### Sampling Schedules

The sampling schedule for the ORSANCO river monitoring network has been planned so that it should be possible to sample each of the selected sites once every 10 days using three full-time field representatives. Each field man is responsible for approximately one-third of the river, but the number of sites assigned to each man is not the same because of varying distances between sites. The station assignments and sampling schedules are shown in Table 2. The code number appearing in Table 1 under the heading, <u>Sampling Schedule</u> indicates the analysis to be performed on each sample. The measurements performed on the 01, 11 and 21 groupings are shown in Table 1.

Samples must be taken at the official site with no deviation. If access to the site is not available for one reason or another (locked gate, high water, icy walk-ways, etc.) the sample may be taken at the nearest convenient point and duly noted on the sampling report form.

# Locations of Sampling Sites

Each sampling site in the ORSANCO monitoring net work is located and briefly described on a page of the navigation charts included in this manual. \*(See II-22 through II-58) for instance, the location of the South Pittsburgh station in the Monongahela River at mile point 5 is described on the navigation chart as "intake to Western Pennsylvania Water Co. . . . . . . . . collected from platform above intake structure."

Samples must be taken at the official site with no deviation. If access to the site is not available, for one reason or another (locked gate, high water, icy walk-ways, etc.) the sample may be taken from the nearest convenient point and properly noted on the sampling report form. (Attachment 1)

#### Securing the Sample

The basic sampling instrument used by the ORSANCO monitoring team is the so-called Ohio River sampler. The original construction of the sampler was of copper because of ease of construction and because at the time (mid-1930's) there was little concern about trace metals in surface waters. Present construction of the bucket is of aluminum with exterior weight in the form of lead plates so that samples may be taken with no detectable metals contamination of the sample. The sampler is designed to accommodate/collection of samples for dissolved oxygen measurement and/or bacteriologi-

# TABLE 1

Analytical Schedule for ORSANCO Primary Monitoring Network Stations \*

Group 01 (Ten Day)	Group 11 ** (Monthly)	Group 21 ** (Quarterly)		
Ammonia Nitrogen	All of Group <u>01</u>	All of Group <u>01</u>		
Tot. Kjeldahl Nitrogen	plus	and Group <u>11</u>		
Nitrate + Nitrite	Barium, total	plus		
Tot. Phosphorus	Cadmium, total	Arsenic, total		
Sulfate	Chromium, total	Selenium, total		
Suspended Solids	Copper, total Silver, total			
Phenolics	Iron, total			
Cyanide	Manganese, total			
	Lead, total			
	Mercury, total			
	Nickel, total			
	Zinc, total			
	Sodium, total			

\* = In addition to the laboratory analyses, each sample is analyzed in the field for temperature, dissolved oxygen, conductivity and pH.

\*\* = The field men are instructed to secure Group <u>11</u> and Group <u>21</u> samples on the first visit of the month and quarter.

# TABLE 2

# ORSANCO Primary Monitoring Network Stations

# (Location, Type, Sample Collector)

				Sam	pling Sche	edule (**)
	River &	Approximate	Type (*)	Ten		
Station Name	Mile Point	Mile Points	Station	Day	Monthly	Quarterly
Oakmont	Alleghenv	13	А	01	11	21
South Pittsburgh	Monongahela	5	A	01	11	21
South Heights	Ohio	15	A	01	11	21
Beaver Falls	Beaver	5	A	01	11	21
East Liverpool	Ohio	40	A	01	11	21
Pike Island	Ohio	84	В	01	11	21
Wheeling	Ohio	87	С			
Shadyside	Ohio	102	A	01	11	21
Willow Island	Ohio	162	В	01	11	21
Lock & Dam #2	Muskingum	6	В	01	11	21
Belleville	Ohio	204	В	01	11	21
Addison	Ohio	260	A	01	11	21
Point Pleasant	Kanawha	21	С			
Winfield	Kanawha	31	A	01	11	21
Gallipolis	Ohio	279	A	01	11	21
Huntington	Ohio	307	A	01	11	21
Kenova	Ohio	316	В	01	11	21
Louisa	Big Sandy	20	A	01	11	21
Greenup	Ohio	341	A	01	11	21
Lucasville	Scioto	15	В	01	11	21
Meldahl	Ohio	436	В	01	11	21
Cincinnati	Ohio	463	A	01	11	21
Little Miami	Little Miami	3	В	01	11	21
Kenton County	Licking	5	A	01	11	21
North Bend	Ohio	490	A	01	11	21
Great Miami	Great Miami	6	A	01	11	21
Warsaw	Ohio	528	В	01	11	2.1
Louisville	Ohio	600	A	01	11	21
West Point	Ohio	626	A	01	11	21
Cannelton	Ohio	721	A	01	11	21
Hawesville	Ohio	728	С			
Sebree	Green	41	В	01	11	21
Evansville	Ohio	791	A	01	11	21
Uniontown	Ohio	846	A	01	11	21
New Harmony	Wabash	52	A	01	11	21
Barkley Dam	Cumberland	31	В	01	11	21
Calvert City	Tennessee	18	A	01	11	21
Joppa	Ohio	952	A	01	11	21

\* = 1 (White)

\* = A - Combined monitor and manual \*\* = See Table 1 for

2 (Hurst) 3 (Lux) B - Manual only
C - Monitor only

\*\* = See Table l for explanation of parameter codes 01, 11 and 21 cal samples. The sampler also provides for a three-fold displacement of water in the DO bottles without aeration. Additional sample volume is secured at the same time to allow for other analyses.

In use, the sampler should have sufficient exterior weight attached to the outside of the bottom to submerge it promptly. In flowing water, an inadequately weighted sampler will float some distance with the current before sinking. Sufficient weight decreases the angle between the line and the vertical so that the depth accuracy is improved. To insure that the sample is taken at the desired depth, the sample line should be marked or knotted at regular intervals so that the sample collector can read the depth of the bucket below the surface.

The interior of the bucket must be kept scrupulously clean. After each sample, the bucket should be emptied and visually inspected for residual debris or oil films that may contaminate the next sample. If contaminated with oil or grease, clean with detergent and rinse thoroughly with water. Good field practice requires that the bucket be rinsed first with the sample being taken, in order to avoid sample-to-sample contamination by abrupt changes in concentrations. In the case of ORSANCO samples, however, where there are no dramatic changes in sample-to-sample concentrations, all samples being taken from the same surface waters, it is sufficient to use the previous sample taken as rinse for the next sample. If the bucket is kept reasonably clean and emptied after each sample, it should not be necessary to obtain a preliminary rinse sample. In the unlikely event, however, that an unusual condition is encountered when a sample is taken, ie., a heavy oil slick or some such condition, the bucket must then be thoroughly cleaned with detergent and rinsed with water before taking the next sample.

Securing the Sample with the Use of the Ohio River Sampler

Place two clean, dry DO bottles in the spring clips mounted in the bottom of the bucket. Position the lid on the bucket so that the dip tubes on the underside of the lid are inserted into the open necks of the DO bottles. Fasten the lid securely in place with the pivoting wing nuts mounted on the flange of the bucket. Lower the bucket into the water to the depth of five to six feet, and wait a sufficient length of time (until bubbling ceases) to insure that the bucket is full. Retrieve the bucket, remove the lid and carefully remove the DO bottles. Promptly stopper the bottles, avoiding entrapment of any air, add the proper identification to the bottles and place in the sample cooler. If a large volume of sample is needed, pour the water remaining in the sample bucket (after removal of the DO bottles) into a larger container and repeat the sampling operation without the DO bottles. The auxiliary sample container should be a plastic container of about two gallons capacity, fitted with a lid to retard spillage. The auxiliary container must also be kept scrupulously clean and rinsed in the same manner as the sample bucket.

Protection of Samples, Dilute Solutions and Field Instruments from Freezing

In the spring, summer and fall months when weather temperatures are normal, no special temperature precautions for protection of the various dilute solutions, samples and instruments are required. In the winter months, however, when air temperatures are below freezing for extended periods of time, there is always the danger of sample and solution loss or instrument damage due to icing and freezing.



During freezing weather, remember that the following events may occur:

- D0 bottles, filled with water at the freezing temperature, exposed at sub-freezing ambient air temperatures will freeze and crack.
- 2. Buffer solutions used for pH standardization will freeze.
- 3. Standard solutions used for conductivity standards will freeze.
- 4. Ampouled preservatives may freeze and crack the container.
- 5. pH electrodes may freeze and crack
- 6. Miscellaneous phenomena

Take whatever sensible precautions are required to forestall the freezing and icing events. Store such equipment in insulated chests, in the heated rear of the

van or in the heated cab of the pick-up truck. Particularly use special care to protect the pH electrode since any damage to this item is a costly one.

It is suggested that the field work required after securing the sample (field measurements, sample preparation, etc.) may be performed under roof at the various sampling sites. While this may not always be possible, it does offer an alternative in some cases.

#### Preservation of Samples

After returning to the vehicle, mix the sample in the auxiliary container, either by stirring or inversion and aliquot the sample to the pre-washed bottles of the proper size according to the determinations to be performed. (cf. Table 3) Any stirring device used to agitate the sample prior to aliquoting should be constructed of an inert plastic material.

Add the proper preservative to each portion as required (Table 3) but do not open the ampoules containing the preservative solutions until immediately prior to use. Note that the constricted neck of the opened ampoule restricts the flow and tapping the inverted ampoule against the neck of the sample bottle may be necessary. Avoid scattering of the preserving solutions; if any of these fluids touch the skin or clothing, flush the area with water. An acid burn of any significance should have medical attention.

Do not try to use a pipette or any intermediate container for transfer of the ampouled solutions to the sample.

#### 3. Shipment of Samples

All samples are to be shipped by Greyhound Package Express to the laboratories to insure delivery to the lab within 24 hours. Any bus shipment, in which a transfer or similar problem is anticipated, is to be shipped by Greyhound's "Next Bus Out" service, where expedited shipment is guaranteed. All samples are to be shipped in styrofoam insulated coolers packed with ice. Delivery arrangements have been made with local delivery services under contract to Greyhound to provide expedient delivery of samples

# TABLE 3A

Sampling Requirements for O1 Group Analysis

Parameter	Bottles	Treatment
TKN Total Phosphorus	l liter	RC, mixed
Total Diss. Solids Fluoride Silica Sulfate Ammonia/N Diss. Phosphorus Nitrate + Nitrite	500 ml	FC
Calcium Magnesium Potassium Sodium	500 ml	ra (hno <sub>3</sub> )
Cyanide	1 liter	R(NaOH)
Phenol	1 liter	$RC(CuSO_4 + H_3PO_4)$

SUMMA	RY								
Вс	ttles	required	-	(3-	1	liter,	)(2-	500	m1)
Pr	eserva	atives	-	HNO	2,9	NaOH,	CuSO	, H	3 <sup>P0</sup> 4

TREATMENT CODE

R	=	Raw
U	=	Untreated
F	=	Filtered
С	=	Chilled
A	=	Acidified

\* Bottle requirements may be altered as required by the laboratories.

# TABLE 3B

# Sampling Requirements for 11 Group Analysis

Paramater	Bottles	Treatment*
Barium, total	l liter	RU, mixed
Cadmium, total		
Copper, total		
Iron, total		
Lead, total		
Manganese, total		
Mercury, total		
Nickel, total		
Zinc, total		

Metals as 1 liter FA, HNO<sub>3</sub> above, dissolved plus parameters as in (see Table 3A) (see Table 3A) <u>O1</u> Group

SUMMARY

Bottles required - Same as for Table 3A, plus 2 - 1 liter Preservative -  $HNO_3$ 

\* See Table 3A for Treatment Code

# TABLE 3C

Sampling Requirements for 21 Group Analysis

Parameter	Bottles	Treatment*
Silver, total Selenium, total Arsenic, total	Use Sample Total metals in <u>11</u> Group	RU, mixed
Silver, diss. Selenium, diss. Arsenic, diss.	Use sample for metals in <u>11</u> Group	FA, (HNO <sub>3</sub> )

Plus Parameters as in <u>Ol</u> Group and <u>ll</u> Group

SUMMARY

Bottles required - same as for Table 3B Preservative - HNO<sub>3</sub>

\* See Table 3A for Treatment Code

# TABLE 3D

# Sampling Requirements for Special Samples

Parameter	Bottles	Treatment*
Radioactivity	l liter	RU
Pesticides	l liter	RU, glass bottle

\* See Table 3A for Treatment Code

from the bus terminals to the laboratory. Shipments arriving at bus terminals during the night are transferred to the laboratories at the start of business on the following day. The sample report form which accompanies each sample is the log-in document which the lab uses to indicate time of arrival at the lab.

# Chain of Custody

Normally, the samples and analytical data obtained by the ORSANCO Monitoring Network do not possess the legal significance requiring a chain of custody protocol. In the event that a situation should arise in which such a formal procedure will be required, the chain of custody procedure recommended by the EPA Regional Office in which the situation arises will be used.

The Surveillance Specialists should note, however, that proper identification of all samples is a vital necessity. Misidentified samples result in confusing data production. Unidentified samples or samples illegibly labeled are simply discarded in the laboratory, resulting in useless field work.

# 4. Analysis Techniques with Field Instruments

Four parameters must be measured as soon as possible after the sample is taken because of their instability. These are conductivity, pH, dissolved oxygen and temperature. Temperature and dissolved oxygen should be run as soon as possible after the sample is taken; pH and conductivity are not as critical but also require measurement in the field. Each of these measurements is affected by ambient air temperature and the necessary precautions and corrections for each must be observed.

The instruments supplied to the field representatives for these determinations have been selected by the ORSANCO staff as being the best suited for the measurements required. However, the best evidence of suitability is performance under the varying and often adverse conditions of actual field use. The Surveillance Specialists are urged to view these instruments critically for signs of fragility, instability, corrosion, chronic maintenance problems and other impediments to efficient field use.

Comments and observations regarding instrument malfunctions or desirable improvements are encouraged.

#### Temperature

The thermometers furnished for the temperature measurements are a Palmer No. 10540 MR, 12 inches in length, calibrated to read in  $1^{\circ}$  divisions from  $-30^{\circ}$  to  $+120^{\circ}$ F; and a Palmer No. 10440 MR, also 12 inches long and calibrated in  $1^{\circ}$  divisions from  $-35^{\circ}$  to  $+50^{\circ}$ C. Both thermometers are supplied in protective metal shields to reduce frequency of breakage and are guaranteed as accurate by the manufacturer to  $+0.5^{\circ}$ .

The Fahrenheit thermometer should be used for calibration of the automatic monitors; the Centigrade thermometer should be used for reporting temperature of the grab samples at the time of collection.

For measurement of temperature of the grab sample, remove the DO samples from the sampling bucket as soon as it is retrieved. Then, with the sample still in the bucket, immerse the stem of the thermometer at least three inches below the surface of the sample and wait about one minute for the temperature to equilibrate. Read the temperature with the thermometer immersed in the sample. Do not remove the thermometer from the sample in order to read it more conveniently.

Report the temperature on the report form to the nearest 0.1°C.

# Dissolved Oxygen

The instrument supplied by ORSANCO for this measurement is the Weston and Stack Model 330 Dissolved Oxygen Analyzer, equipped with a Model 33 Lab Probe. (The lab probe is designed with a built-in agitator to provide the necessary sample flow.) Each Surveillance Specialist must be familiar with the details of operation and routine maintenance following the procedure put forth in the instruction manual supplied with the instrument.

The DO meter should be standardized daily, or in the case of intermittent operation, before use. Use the standardization procedure outlined in the Weston and Stack Manual, employing the Winkler method. The "wet bottle" standardization, which is not outlined in the Weston and Stack instruction manual, may also be used as follows:

- 1. Place about 100 ml of distilled water in a standard D0 bottle; stopper and shake vigorously.
- 2. Remove the stopper and insert the probe, taking care not to wet the tip of the probe.
- 3. Note the temperature of the air phase in the bottle, as indicated on the Model 330 meter. Switch the meter to the high DO range and adjust the reading according to the following table:

Temperature ( <sup>O</sup> C)	Oxygen (mg/1)
20	9.2
21	9.0
22	8.8
23	8.7
24	8.5
25	8.4
26	8.2
27	8.1
28	7.9

The probe is now standardized for future readings, but should be calibrated daily. An occasional check of the wet bottle against the Winkler calibration is recommended.

To obtain a DO reading on the sample, remove the DO bottles containing a fresh sample from the sampling bucket as soon as it is retrieved. (Stopper the bottles and return to the vehicle.) Insert the probe into the bottle and note the DO reading using the high range scale, reading the result to the nearest 0.1 mg/1. Also, note the sample temperature as indicated by the meter as a cross check on the sample temperature as observed with the glass-stemmed mercury thermometer. Record the result on the report form. If the sample on which the DO measurement was obtained is to be used for a BOD measurement, and if the DO is less than 9.2 mg/l, dribble a few drops of distilled water from a squirt bottle into the neck of the DO bottle to replace the small loss caused by probe displacement. Restopper the bottle and place it in the cooler for shipment to the laboratory.

pH

The instrument used for the ORSANCO pH measurement is the Leads and Northup Model No. 7417 Portable pH meter with an Ingold combination probe No. 27617-02

As with the other ORSANCO field instruments, it is the responsibility of the Surveillance Specialists to be familiar with the manufacturers directions for use and maintenance of these instruments.

Follow the manufacturer's instructions for standardization of the meter; however, to improve accuracy of readings, standardize the meter at two levels using both the pH 4.0 and pH 7.0 buffers. Discard the buffer solutions used for the standardizations; use fresh solutions each time the meter is standardized.

Abnormal instrument behavior, such as a wildly twitching needle, slow drift or erratic response, may be indicative of various instrument failures such as a cracked electrode, weak battery, loss of KCl in the reference electrode, faulty electrical connection, etc. The battery check position of this instrument does not check all batteries. Such behaviors are most likely to be observed during the standardization operation. Refer to the manual for troubleshooting or return the meter to the ORSANCO office for repairs.

Note the temperature of the sample and adjust the temperature <sup>O</sup>C compensator to the measured temperature. Pour an aliquot of the fresh grab sample into the vessel reserved for pH measurement, and with the meter on standby, rinse the electrode by gently raising and lowering the container several times. Discard that portion of the sample and pour a fresh aliquot into the vessel. With the meter on pH, immerse the electrode into the sample and read the pH to the nearest 0.1 unit. Record the result on the report form. Rinse the electrode with distilled water and store until the next sample.

# Conductivity

The instrument used for the conductivity measurement is the Solu Bridge RRB-3 portable battery operated meter, equipped with a CEL-VS 2 dip cell. Details of operation, maintenance and troubleshooting are contained in the manual supplied with the instrument.

The conductivity cell supplied with the instrument has a stated cell constant of 2.0. The cell is very stable, barring accident or sample damage, and does not require standardization. However, the cell should be checked daily with the two standard conductivity solutions supplied by the ORSANCO office. These solutions have conductivities of 200 and 1200 umhos.

Pour the standard solution into the container reserved for conductivity readings. Place the cell in the solution and move it up and down vigorously under the liquid to insure removal of air bubbles from the cell casing. Discard the solution, place fresh solution in the container and repeat the operation. Take the conductivity measurement with the cell immersed in the solution to a point at least 0.5 inches above the uppermost air vent and no closer than 0.5 inches to the sides and bottom of the container. Apply the necessary temperature conversion for adjusting the reading to  $25^{\circ}$ C. Temperature compensation is necessary because the stated conductivity of the standard solutions implies reading at  $25^{\circ}$ C. The cell readings, using the 200 and 1200 umho/cm standards should agree within + 3 percent.

If the cell constant appears to have changed, a new constant may be calculated following the procedure outlined in <u>Standard Methods</u>, 14th Edition, pp. 72 and 73. A damaged cell should be replaced with a new one.

Using an aliquot of fresh grab sample, rinse the cell with one or more portions, as described in the previous paragraph. Measure the resistance of the sample using the proper temperature compensation as outlined in the manufacturer's manual. Record the result on the report form.

# 5. Maintenance of Automatic Monitor Equipment

See Appendix 5 of "Quality Control Assurance Program for Primary In-stream Monitoring Network".

## 6. Special Samples

A proposal has been made for ORSANCO to establish a protocol for determining the presence and concentration of pesticides and herbicides in the river water and sediments and to measure present levels of radioactivity in the waters.

The sampling requirements for pesticides and radioactivity in water are listed in Table 3D. No listing has been made for sediment sampling, pending further discussion concerning available methods.

The analytical procedures to be used will be those recommended by the U. S. EPA when the special sample program is initiated.

# ORSANCO WATER QUALITY SAMPLE REPORT

Station Name		Stat	ion	I.D. Code		
Stream	1	Mile Point		Collect	ion	Time
Analyses Code _		Analysis Ex	cept	ions		
Type Sample	Routine Grab	Other		F	ield Techni	ician
Comments:						
commences.						
FIELD DATA		River Con	ndit	ions		
Water Temperature (C <sup>O</sup> )	) 1A	Weather				
Conductivity (µmhos/cm)	1B			LAB USE	ONLY	
pH (su)	1C	Date Received		Lab	Number	
Dissolved		at Lab			Time	ising
Oxygen(mg/1)	1D	Date Completed	d		Che	mist
CENEDAT		NUTDIENTO (			TOTAL NET	ATC ( /1)
SENEKAL	24	Total Phone	L) F		Ancest	ALS (JIG/1)
FLOW(CFS)	20	phorous (P)	3A		Arsenic	4A
Suspended	20	TKN	3B		Barium	48
Solids (mg/l) Dissolved	20	Ammonia	3C		Cadmium	40
Solids (mg/l)	20	Nitrate	3D		Chromium	4D
Acidity (mg/l)	ZE	Dissolved Phos- phorous	3E		Copper	4E
Alkalinity(mg/l)	)2F	BACTERIOLOGICA	L		Iron	41
Sulfate(mg/1)	2G	Total Coliform			Lead	46
Chloride(mg/1)	2H	(#/100ml) 5A Fecal Coliform	4		Manganese	4H
Fluoride(mg/1)	2J	(#/100m1)	5B		Mercury	4J
hess (mg/I)	2K	BOD5 (mg/1)	5C	•	Nickel	4K
Calcium (mg/1)	2L				Selenium	4L
lagnesium(mg/l)	2M				Silver	4M
Sodium(mg/1)	2N		_		Zinc	4N
Potassium(mg/1)	2P		_			
Silica(mg/l)	2Q		_			_
Phenolics(µg/1)	2R		_			_
			[	1 1 1 1		
Cyanide(mg/1)	25					

# USE OF WATER QUALITY REPORT FORM

The ORSANCO water quality sample report form is to be used in accordance with the following:

Station Name - The station name should be entered on all forms used. Names for regular stations with I D numbers assigned should remain uniform.

Station I D Code - This is the four digit code used at ORSANCO to identify stations to the computer. The first digit is the station type code. 1 is used for routine grab samples. The second digit is a state code. The third and fourth digits are station identifiers. Forms and samples from locations where routine samples have not been collected will not use this column, but will have the stream and mile point identified. (Details on next page)

Stream and Mile Point - May be omitted when station I D code is used.

<u>Collection Date and Time</u> - Numbers only should be used for the date; such as, 7-01-76. For the time, military time, time zone, and daylight or standard time should be entered; for example, 1415 CDT.

Analyses Code - Two digit code to be used. (See attachment)

<u>Analysis Exceptions</u> - Any exceptions to the standard analyses should be noted (identified by their codes) by marking <u>add</u> and the two digit alpha numeric parameter code/s and/or delete and the parameter code/s.

Type Sample - Either routine grab or other box should be checked and type sample specified in blank provided.

Field Technician - Form should be signed by person responsible for the collection and preservation of the sample.

<u>Comments</u> - This column is reserved for any comments or unusual conditions noted by sampler or special instructions to lab.

River Conditions - Flow and general river conditions should be noted, as well as unusual conditions.

Weather - Weather conditions and approximate air temperature at time of sample collection should be noted.

Field Data - Field readings to be recorded on sheet.

White copy of this form should accompany sample to lab. Lab will complete and forward to ORSANCO.

Pink copy should be forwarded to ORSANCO office by sampler.

Yellow copy may be retained by sampler for his records.

# STATION ID CODE DESIGNATIONS

# First Digit

O indicates water users data, pre-1972 U.S.G.S. data, or special reports from discharges data received during the Demo Project (1969-71).

l indicates manual sample collected in accordance with the ORSANCO Monitoring Strategy

# Second Digit

This digit is a state code for sampling location.

1	- New York
2	- Pennsylvania
3	- Virginia
4	- West Virginia
5	- Ohio
6	- Kentucky
7	- Indiana
8	- Illinois

# Third Digit

Sampling point identification code relating to sampling location.

00-29 -Main stem Ohio River location 30-99 -Tributary location

II-17

# •

# ANALYSIS SCHEDULES

Analysis Schedule 01 (USGS Schedule 406 after 3/1/76)

Cyanide	25
Ammonia Nitrogen	3C
Nitrite + Nitrate	3D
TKN	3B
Total Phosphorous	3A
Sulfate	2G
Phenolics	2R
Suspended Solids	2C

Analysis Schedule 11 (USGS Schedule 407 after 3/1/76)

All analyses of analyses schedule Ol plus:

Barium	4 B
Cadmium	4C
Chromium	4D
Copper	4E
Iron	4 F
Lead	4G
Manganese	4H
Mercury	4J
Nickel	4K
Zinc	4N
Sodium	2N

Analysis Schedule 21 (USGS Schedule 408 after 3/1/76)

All analyses of analyses schedule 11 plus:

Arsenic	4A
Selenium	4L
Silver	4M

# STATION CODES FOR UPPER OHIO REGION MANUAL MONITORING STATIONS

Allegheny River at Oakmont, Pa.	1233
Monongahela River at South Pittsburgh, Pa.	1237
Ohio River at South Heights, Pa.	1201
Beaver River at Beaver Falls, Pa.	1242
Ohio River at East Liverpool, Oh.	1500
Ohio River at Wheeling, W. Va. (Pike Island Dam)	1405
Ohio River at Shadyside, Oh.	1521
Ohio River at Willow Island, W. Va.	1408
Muskingum River at Lowell, Oh.	1531
Ohio River at Belleville Dam, W. Va.	1421
Ohio River at Addison (Kyger Creek), Oh.	1510
Ohio River at Gallipolis Dam, W. Va.	1422

# STATION CODES FOR MIDDLE OHIO REGION MANUAL MONITORING STATIONS

Kanawha River at Winfield, W. Va.	1450	
Ohio River at Huntington, W. Va.	1412	
Ohio River at Kenova, W. Va. (South Point, Oh.)	1523	
Big Sandy River near Louisa, Ky.	1630	
Ohio River at Greenup Dam, Ky.	1621	
Scioto River at Lucasville, Oh.	1538	
Ohio River at Meldahl Dam, Oh.	1511	
Ohio River at Cincinnati, Oh.	1504	
Little Miami River at Cincinnati, Oh.	1571	
Licking River at Covington, Ky.	1634	
Ohio River at North Bend, Oh.	1508	
Great Miami River at Cleves, Oh.	1551	
Ohio River at Markland Dam, Ky.	1600	

# STATION CODES FOR LOWER OHIO REGION MANUAL MONITORING STATIONS

Ohio River at Louisville, Ky.	1601
Ohio River at West Point, Ky.	1622
Ohio River at Cannelton Dam, Ind.	1721
Green River at Sebree, Ky.	1656
Ohio River at Evansville, Ind.	1703
Ohio River at Uniontown Dam, Ind.	1722
Wabash River at New Harmony, Ind.	1741
Cumberland River at Barkley Dam, Ky.	1645
Tennessee River at Paducah, Ky.	1650
Ohio River at Joppa, Ill.	1821




















A STATE OF THE STA Hoges Landing Lich. & Davmark 259.0 CHART NO THE from platform over intake structure to son, Ohio M.P. 260.0 (sample collected Automatic - Intake to Kyger Creek Power Generating near Addison, Ohio M.P. 260.0 (tap in - Kyger Creek Power Generating Plant of Ohio Valley Electric Corp. near Addi-Plant of Ohio Valley Electric Corp. Gp. Fl. W. OHIO RIVER 4000 raw water line next to pumps). Monitoring Site SCALE. 1" - 2000' 2 I GALLIPOUS DAM ELEV 534 и 1 2 нини 1 plant). +260. AL POOL  $\odot$ Station normal pool. Lower guide wall removed to 12/feet below beartrap piers, and fixed weir removed to 15 1st below Old U. S. Lock & Dum No. 25, Mile 260.7, river wall. - Manual below normal pool. Abutment I foot below normal pool. .Towe 4 /001 York  $\Theta$ 5 Jose Ky normal pool. Land wall and upper guide wal II-32 260.7 F. R. Dam 25 Light WEST VIRGINIA MASON COUNTY +261 OHIO RIVER, ADDISON, OHIO MP 260.0 5 411.4 31111 NOTE: 0 ATCH LINE 144 Campaign Bend Light 261.7 F. G. GALLIA COUNTY 5 01H0 Town Addison Campaigner Marine Ways Heights B

















SCIDTO RIVER, LUCASVILLE, OHIO MP 15

KENTUCKY OHIO RIVER

0 1 2 3 4000' НННН1 1 2 3 4000' SCALE: 1" = 2000' СНАRT NO. 124

















Light & Daymer: 622.8 F. R. CHART NO. 70 ACOO. OHIO RIVER SCALE: 1"=2000' OHIO RIVER, WEST POINT, KENTUCKY MP 625.9 2 and 1 2 +623 Brinney Creek - 1625 NORMAL POOL CANNELTON DAM ELEV 383.0 624 CHANNEL LINE -Automatic - Intake to Mill Creek Power Generating JEFFERSON COUNTY - Intake to Mill Creek Power Generating KENTUCKY Plant of Louisville Gas and Electric Plant of Louisville Gas and Electric Co. near West Point, Ky. M.P. 625.9 (tap in raw water line [cooling] at Co. near West Point, Ky. M.P. 625.9 (sample collected from walkway over Monitoring Site toris 67-II Enersole intake to plant). . (sdmud HARRISON COUNTY INDIANA -Manual Creek Will Fishtown Light 625.7 C +626 0















Automatic - Intake to B. F. Goodrich Chemical Co. Plant near Calvert City, Ky., M.P. 18 (tap in raw water line ------ Ashland Oil Co. Terminal Docks M.P. 6.0 (sample C ..... Chattes Creek Links collected from terminal pier at upstream end). ( . ... FI.W. 2 Ser.  $(\mathbf{e})$ 10.3 ( LIVINGSTON COUNTY 11 Scale I Inch . | Wile 0.... Monitoring Site LINN IOOUT TENNESSEE RIVER, CALVERT CITY, Little Chain Light 17.8 0 MP 6, MP 18 Lin Fl.W., 2 scc. to chemical plant). ailine KENTUCKY Creek 20 3 Haddock Ferry Light 16.6 & E Mooring Cell A B B -Manual TAO 6 0 Hart TAN 67 20 cr Course Line 200 C LIVINGSTON COUNTY 2 MARSHALL COUNTY KENTUCKY No Celle Ð, Diffusion Outfall Pipe No. 0 NORMAL POOL DAW NO. 32 E. 301, 7 (1929 DAW NO. 32 GEN. 401, ) (2) 0 Lieht and Daymark Sec. 2 Aashes Big Chain Light 15.3 0 FI.W., 2 Rec. 932.5 GP.F. 50 5 932 0 WAL POOL DAM NO. 52 WAL POOL DAM NO. 52 01.7 (1929 GEN. ADJ.)\* 20 20


APPENDIX 3 Analytical Methods -- Storet Parameter Codes, References and Reporting Levels

			REFERENC	E AND PAG	E NUMBER		
PARAMETER AND REPORTING UNITS	STORET AND PARAMETER CODE	ANALYTICAL METHOD	U.S. EPA 1974	ST. METHODS 14th EDITION	ASTM PART 31 1975	NSGS	REPORT- ING LEVEL
BASIC PHYSICAL AND CHEMICAL							
Temperature, °C	00010	Calibrated Glass or Electric Thermometer	286	125		31	x.
pH, Units	00400	Electrometric Measurement					×.
Dissolved Oxygen, mg/l	00300	Winkler (Azide Mod.) or Electrode Method					x.x
Conductivity, micromhos	00095	Wheatstone Bridge	275	71	120	148	х.
Turbidity, NTU	00070	Nephelometric	295	132	223	156	х.
Flow, CFS	00060	USGS Gauge					
GENERAL CHEMICAL							
Acidity, $mg/1$ as $CaCO_3$	00435	Elec. End Point (pH 8.2) or Phenol-Phthalein	1	273(4d)	116	40	x.
Alkalinity, mg/l as CaCO <sub>3</sub>	00410	Elec. End Point (pH 4.5) Manual Or Automated or Equiv. Auto. Methods	3/5	278	111	41	×.
BOD, 5 day, mg/l	00310	Winkler (Azide Mod.) or Electrode Method					х.
Cyanide, mg/l	00720	Distillation, Followed by Colorimetric Barbituric Acid or Pyridine Pyrazalone					xx.
Fluoride, mg/1	00950	Distillation, Followed By Electrode, SPADNS or Automated Complexone					xx.

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			REFERENC	E AND PAG	E NUMBER		
PARAMETER AND REPORTING UNITS	STORET AND PARAMETER CODE	ANALYTICAL METHOD	U.S. EPA 1974	ST. METHODS 14th EDITION	ASTM PART 31 1975	USGS	REPORT- ING LEVEL
GENERAL CHEMICAL (cont.)							
Total hardness, mg/l as CaCO <sub>3</sub>	00600	EDTA Titration, Auto. Colorimetric or Atomic Absorption (Ca + Mg)					х.
Ammonia, mg/l	00610	Distillation at pH 9.5 Followed by Nesslers, Titration, Electrode or Auto.	159/165 168	412; 616	237	116	xx.
Nitrate/N, mg/l	00620	Cadmium Reduction; Brucine Sulfate or Automated Method	201;197 207	423; 427 620	358	119	xx.
Total Kjeldahl/N, mg/l	00625	Digestion, distillation, Nessler, Titration, Electrode or Auto. Rhenolate	175,182	437		122	×
Phenolics, mg/l	32730	4AAP, Colorimetric	241	582	545		xxx.
Total dissolved phosphorus, mg/l	00666	0.45µ Filtration FBRP for total Phosphorus	249,256	476 <b>,481,</b> 624	384	133	xx.
Total phosphorous, mg/l	00665	Digestion, Colorimetric, Manual or Auto.	249,256	476,481, 624	384	133	xx.
Solids, dissolved, mg/l	70300	Glass Fiber Filtration, 160° C	266	92			х.
Solids, suspended, mg/l	70299	Glass Fiber Filtration, 103 to 105° C	268	94			х.
Sulfate, mg/l	00945	Gravimetetric; turbidimetric or Auto.	277, 279	493, 496	424, 425		х.
Sodium, mg/l	00630	AA or Flame Photometric	147	250	403	143	x.

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					and a state of the	2	
			REFERENC	E ANU PAG	E NUMBER		
PARAMETER AND REPORTING UNITS	STORET AND PARAMETER CODE	ANALYTICAL METHOD	U.S. EPA 1974	ST. METHODS 14th EDITION	ASTM PART 31 1975	NSGS	REPORT- ING LEVEL
GENERAL CHEMICAL (cont.)							
Potassium, mg/l	00935	AA or Flame Photometric	143	235,234	403	134	x.
Silica, Dissolved, $mg/l$ as $SiO_2$	00955	0.45 µ Filtration, Colorimetric	274	487	398	139	×.
Calcium, Dissolved mg/1	00915	0.45µ Filtration, AA	103	148, 189	345	66	x.
Magnesium, Dissolved, mg/l	00925	0.45µ Filtration, AA	114	148, 221	345	109	x.
Total Organic Carbon, mg/l	00680	Combustion-Infrared Method	236	532	467	4	х.
TRACE METALS							
Arsenic, Total, mg/1	01002	Digestion, SDDC Colorimetric; or AA	995	285,283 159			xxx.
Arsenic, Dissolved, mg/1	01000	0.45µ Filtration, FBRM <sup>+</sup>					XXX.
Barium, Total, mg/l	01007	Digestion, AA	67	152			· xxx
Barium, Dissolved, mg/l	01005	0.45 µ Filtration, FBRM <sup>+</sup>					xxx.
Cadmium, Total, mg/l	01027	Digestion, AA or Colorimetric	101	148,142	345	92	. xxx
Cadium, Dissolved, mg/1	01025	0.45 µ Filtration, FBRM <sup>+</sup>					xxx.
Chromium, Total, mg/l	01034	Digestion, AA or Colorimetric	105	148,192	345,286	78,77	, XXX
Chromium, Dissolved, mg/l	01030	0.45 µ Filtration, FBRM <sup>+</sup>					XXX.
Copper, Total, mg/l	01042	Digestion, AA or Colorimetric	108	148,196	345,293	83	. xxx
Copper, Dissolved, mg/1	01040	0.45 µ Filtration, FBRM <sup>+</sup>		ł			xxx.

FBRM = followed by referenced method III-3

			REFERENC	CE AND PAG	GE NUMBER		
PARAMETER AND REPORTING UNITS	STORET AND PARAMETER CODE	ANALYTICAL METHOD	U.S. EPA 1974	ST. METHODS 14th EDITION	ASTM PART 31 1975	NSGS	REPORT- ING LEVEL
TRACE METALS (cont.)							
Iron, Total, mg/1	01045	Digestion, AA or Colorimetric	110	148,208	345,326	102	. XXX
Iron, Dissolved, mg/1	01046	0.45 $\mu$ Filtration, FBRM <sup>+</sup>					xxx.
Manganese, Total, mg/l	01055	Digestion, AA, or Colorimetric	116	148,225	345	111	ххх.
Manganese, Dissolved, mg/l	01056	0.45 µ Filtration, FBRM <sup>+</sup>		177			xxx.
Mercury, Total, mg/l	71900	Digestion, Flameless AA	118	156	338		xxxx.
Mercury, Dissolved, mg/l	71890	0.45 $\mu$ Filtration, FBRM <sup>+</sup>					xxxx.
Lead, Total, mg/l	01051	Digestion, AA or Colorimetric	112	148,215	354	105	.xxx
Lead, Dissolved, mg/l	01049	0.45 $\mu$ Filtration, FBRM <sup>+</sup>					.xxx
Nickel, Total, mg/l	01067	Digestion, AA or Colorimetric	141	148,232	345	115	. XXX
Nickel, Dissolved, mg/l	01065	0.45 µ Filtration, FBRM <sup>+</sup>					xxx.
Selenium, Total, mg/l	01147	Digestion, AA	145	159			.xxx
Selenium, Dissolved, mg/l	01145	0.45 $\mu$ Filtration, FBRM <sup>+</sup>					xxx.
Silver, Total, mg/l	01077	Digestion, AA or Colorimetric	146	148,243		142	xxx.
Silver, Dissolved, mg/1	01075	0.45 $\mu$ Filtration, FBRM <sup>+</sup>					xxx.
Zinc, Total, mg/l	01092	Digestion, AA or Colorimetric	155	148,265	345	159	.xxx
Zinc, Dissolved, mg/1	01090	0.45 µ Filtration, FBRM <sup>+</sup>					XXX.

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			REFEREN	CE AND PA	GE NUMBER		
PARAMETER AND REPORTING UNITS	STORET AND PARAMETER CODE	ANALYTICAL METHOD	U.S. EPA 1974	ST. METHODS 14th EDITION	ASTM PART 31 1975	NSGS	REPORT- ING LEVEL
TRACE METALS (cont.)							
Trace Metals Not Listed		+=Followed By kecommended Procedure	*				
RADIOLOGICAL							
Alpha, Total, pc/l	01501	Proportional or Scintillation Counter		648	591		×.
Alpha, Dissolved, pc/l	01503	0.45µ Filtration, Proportional or Scintillation Counter		648			x.
Alpha, Counting Error, pc/l	01502	Proportional or Scintillation Counter		648	594		
Beta, Total, pc/l Beta, Dissolved, pc/l	03501 03503	Proportional Counter 0.45µ Filtration, Proportional Counter		648	601		x. x.
Beta, Counting Error, pc/l	03502	Proportional Counter		648	606		
Radium, Total, pc/1	09501	Proportional or Scintillation Counter		661	661		x.
Radium, Total, Counting Error, pc/1	09502	Proportional or Scintillation Counter		661			
Presticides, ug/l and other Organics		Extraction, GC Method	* *	555	529	24	xx.
BACTERIA		*Proceedure as specified by EPA					
Coliform, FECAL, No/100 ml	31616/31615	MPN; MF		922, 937		45	

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	REPORT- ING		
	nsgs	20 32	
	ASTM ASTM PART 31 1975		
	ST. ST. METHODS 14th EDITION	922,928, 916,928 943,944 947	
	U.S. EPA 1974	4767 47	
1	ANALYTICAL METHOD	MPN; MF MPN; MF with Enrichment MPN; MF; Plate Count	9-111
	STORET AND PARAMETER CODE	31501/31506 31671/31675 31672	
	PARAMETER AND REPORTING UNITS	BACTERIA (cont.) Coliform Fecal in Presence of Chlorine, No/100 ml Coliform, Total, No/100 ml Coliform, Total, in Presence of Chlorine, No/100 ml Fecal Strep., No/100 ml	

# Protocol for Quality Control of Data in ORSANCO Contract Laboratories

U. S. G. S. Laboratories

In the past, analytical services have been provided to the ORSANCO monitoring network by the laboratories of the U. S. Geological Survey, particularly the Albany, and Atlanta Regional Laboratories. Quality Control in these laboratories is practiced as follows:

On a daily basis, a blind reference sample is added by the quality control officer to each batch of incoming samples. The resulting analytical data is reviewed and the necessary adjustments are made, if a variance is observed. When a variance is observed, samples are either re-run or the data is discarded. Also on a daily basis, a known standard for each parameter is run at the beginning and end of each set of samples or with a frequency of one standard to every 15 samples to insure replication.

The U. S. EPA-EMSL reference samples for nutrient elements, COD, etc., are used as supplements to the U.S.G.S. reference samples daily or periodically as required. Once a week, or more often if the sample load is unusually heavy, a trace metals reference sample is used as a blind. The same corrective measures are used with the mineral type reference samples.

The mineral samples routinely used as reference samples contain the conventional mineral constituents and are prepared by the U.S.G.S.-WRD Laboratory in Denver Laboratory; a smaller number of special reference samples (mercury, nutrients, BOD, COD, etc.) are available from EPA-EMSL.

In addition, other techniques are also used, such as interchange of samples between district and project laboratories, analysis of reference samples submitted by the Water Resources District laboratories to all U.S.G.S. labs, etc. The use of an appointed quality control officer in each laboratory is emphasized.

## State and Other Laboratories

Analytical services furnished by contract to ORSANCO, either by private consulting laboratories or by State laboratories, will require the following as a part of the laboratory's quality control effort:

- 1. Minimum Daily Quality Control
  - A. After a standard reagent curve composed of a reagent blank and at least three standards have been prepared, a daily check of the standard curve are to be run using at least a reagent blank and one standard at mid-range of the working curve. Daily checks must be within <u>+</u> 10 percent of the original curve.
  - B. If 20 or more samples per day are analyzed, verify the working standard curve by running an additional standard at mid-range every 20 samples. Checks must be within + 10 percent of the original curve.

- C. Run at least one duplicate sample and one spike every 10 to 20 samples or with each set of samples to verify the precision of the samples. Checks must be within <u>+</u> 2 standard deviations.
- 2. Routine, Non-daily Quality Control
  - A. The laboratory must perform on a known reference sample (when available) once per quarter for the parameters measured. The measured value should be within <u>+</u> 2 standard deviations of the known value as based upon the precision given in the approved method.
  - B. The laboratory must perform on an unknown performance sample (when available) once per year for the parameters measured. Results must be within <u>+</u> 2 standard deviations for precision in the approved methods. If problems do occur, appropriate technical consultation will be provided and a follow-up performance sample will be analyzed
  - C. Standard deviation  $(\tau)$  should be calculated and documented for all measurements being conducted.
- 3. If more than five persons are employed in the laboratory (other than the supervisor) one person will be appointed as the quality control officer, whose responsibility it will be to become familiar with quality control techniques and programs and who will conduct the quality control program in the laboratory.
- 4. The quality control officer will keep a complete log of all quality control samples and data. All such information will be available for inspection.
- 5. Other items that will be strongly recommended to the contract laboratories will be: a) the use of service contracts on analytical balances; b) use of class S weights for periodic checks on balances; c) use of an NBS standardized thermometer to check thermometers in ovens, water baths, etc.; d) color standards for spectrophotometer checks and e) use of quality control charts.

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MAINTENANCE AND SERVICE OF AUTOMATIC QUALITY MONITOR\*

V

#### Introduction

A disciplined and rigorous maintenance program is the key to obtaining valid and useful data from the operation of automatic field instrumentation. For the Robot Monitor, this program must be carried out with diligence to assure:

- 1) That an adequate flow of sample water is obtained through the flow system at all times.
- That sensors are free of dirt and contaminants which may decrease their sensitivity or accuracy.
- That the electronic circuitry is functioning properly and with good stability.
- That the calibrations of the parametric systems and the recording equipment are maintained.
- 5) That functional failures of electromechanical and mechanical phases of the system are averted by preventive maintenance procedures.

While the desirability of achieving goals (1) and (2) is obvious, the accomplishment can sometimes be exceedingly troublesome. However, any effort that may be required must be provided.

Points (3) and (4) are not quite so vital and are usually somewhat less troublesome, but are important since they determine the quality of the data and influence the confidence with which it will be accepted.

#### Maintenance Schedules

Monitor station service calls for cleaning and operation checking will be required at a frequency determined by local stream conditions and influenced by seasonal variations in flow. Experience is essential to decide the exact need for attention at each monitor location in each season. However, optimum performance will require a 7 to 10 day schedule.

#### Service Log

Field personnel will maintain a service log for each monitor. This record consists of an assembly of individual Service Call Reports containing pertinent comments relating to stream conditions and instrumentation problems. The log should also include records of repair work and basic calibration that may be done away from the monitor site.

The complete log is useful, (a) in evaluation of unusual or question-

\* Procedures outlined for maintenance and service of the automatic monitors are based on instructions furnished by Schneider Instrument Company, 8115 Camargo Road, Cincinnati, Ohio 45243 able data, (b) for more accurate determination of cleaning requirements on a seasonal and location basis, (c) for anticipation of the need for sensor replacement, (d) as a troubleshooting tool, and (e) as a record of what has been done and what may have been neglected. The log is a means for better system performance and an aid in evaluation of system data output.

# Procedure for "Weekly" Service (Cleaning and Operation Checking)

The procedure is subdivided into four general headings for reference; however, there is no exact dividing line between areas of activity. The individual steps are arranged to permit the most orderly progression through the work and to minimize the elapsed time required.

Initial Observation

1) Before disturbing the monitor in any manner, read and record the panel meter indication for each parameter. Be certain to properly interpret the meter scale divisions.

2) Read and record the telemeter line current.

3) Open the telemeter cubicle rear door and switch the test signal to the 0100 level. Do not leave the door open.

4) Observe the flows through the effluent line. Make a record of any abnormal flow conditions.

5) Open the flow cell drawer; try to avoid causing any change in flow. Observe the flow through each cell and make a record of any abnormal flow conditions in particular flow cells.

Cleaning

1) Remove the temperature/dissolved oxygen sensor assembly; the temperature sensor shares a flow cell with the dissolved oxygen sensor assembly. Observe the condition of the membrane and of the DO electrode. If unusual slime build-up or algae growth exists, note this on the service call report. The sensor systems are expected to get dirty and it will take some field experience to recognize the difference between normal and unusual conditions.

2) Gently wipe the DO electrode membrane with wet soft tissue; do not clean with any abrasive material or use any tool which may injure the membrane. Wipe and rinse the membrane repeatedly as required until it is entirely clean. A squirt bottle of distilled water (or tap water) may be useful in this operation.

3) Use wet tissue to thoroughly clean the entire body of the DO electrode, the temperature compensator, the temperature sensor, and the underside of the neoprene stopper. Clean the top of the sensor assembly with moist tissue and dry carefully with clean dry tissue.

4) Clean the temperature/dissolved oxygen flow cell using the plastichandled sponge mop provided for this use. Use the tubing brush provided to clean the outlet line from the flow cell.

5) Return the temperature/dissolved oxygen sensor assembly to its flow cell.

6) Remove the conductivity sensor assembly. Observe the condition of the vertical and horizontal bores in the conductivity cell. If unusual slimebuild-up or algae growth exists, note this on the service call report.

7) Clean the vertical and horizontal bores of the conductivity cell using wet 8-mm tubing cleaner. For the low-range cell (K=1, black body) use a double strand running the folded end into the cell. This cell has a platinum black surface which will be damaged if the sharp end of the wire in the tubing cleaner is run across it. Using a plentiful supply of water on the tubing cleaner and moving it slowly and gently, pass it into or through each bore several times. A squirt bottle of distilled water (or tap water) will be useful in this operation. Vigorous manipulation of the cleaner is not required and may cause damage to the cell. Under no circumstances, in the field, should the conductivity cell be cleaned chemically, under power, or with any mechanical abrasive device.

8) Use wet tissue to throughly clean the entire body of the conductivity cell, the temperature compensator, and the underside of the neoprene stopper. Clean the top of the sensor assembly with moist tissue and dry with dry tissue.

- 9) Clean the conductivity flow cell and flow cell outlet line.
- 10) Return the conductivity sensor assembly to its flow cell.

11) Remove the pH sensor assembly. Observe the condition of the sensitive tip of the glass electrode and the orifice end of the reference electrode. If unusual slime build-up or algae growth exists, note on the service call report.

12) Gently wipe the tips of the glass electrode and the reference electrode with wet soft tissue. Use extreme care when handling the glass electrode and avoid a twisting action during wiping; the glass ball tip can be twisted off very easily. A squirt bottle of distilled water (or tap water) may be useful in this operation.

13) Use wet tissue to thoroughly clean the entire bodies of the glass and the reference electrodes, the temperature compensator, the ground rod, and the underside of the neoprene stopper. Clean the top of the sensor assmebly with moist tissue and dry carefully with clean dry tissue.

14) Check the electrolyte level in the reference electrode. If it is within 3/4 inch above the bottom of the reservoir, then refill to within 1/2 inch of the filler hole with Beckman #4787 reference electrode filler solution. CAUTION: Use no other solution in the reference electrode.

15) Clean the pH flow cell and flow cell outlet line.

16) Return the pH sensor assembly to its flow cell.

- 17) Wait at least five minutes after the replacement of the last sensor assembly for transients to subside, then read and record the panel meter indication for each parameter. These readings are "after cleaning" and will provide some indication of the effect of sensor cleaning. However, it must be considered quite possible that some parameter values may have changed during the time between the initial reading and the completion of the sensor cleaning.
- 18) Turn the flow control valve in the flow cell drawer to the OFF position. Place the plastic basin on the floor at one side of the drawer to catch waste water. Remove the cleanout plugs from the flow cells on that side one at a time, and run the tubing brush through each line and into the inlet reservoir. The flow control valve can be opened briefly after each line is cleaned to flush it out. Replace the plug after each line is cleaned, tightening it only enough to prevent leaks-This can be done by hand. Repeat for the flow cells on the other side.
- 20) After five minutes, review the parameter readings comparing them to the "after cleaning" readings already recorded. Give special attention to the DO reading, since an increase may be an indication of inadequate flow before adjustment. If there is a change, record it on the service call report. The monitor sample flow must not drop to a borderline level between weekly cleanings. If such a situation should arise, the reason for flow decrease must be corrected.

#### Operation Checking

- 1) For each analyzer the following steps should be performed:
  - a) Open the control access door on the front panel of the analyzer.
  - b) Press the push button switch (left side of the sub-panel).
  - c) Put the toggle switch (right side of the sub-panel) in the down position.
  - d) Read the panel meter; it should indicate the reading of the lowscale calibration reference. Record this reading on the service call report. NOTE: The low-scale calibration reference point and the high-scale calibration reference point are marked on the front sub-panel of each analyzer as the labels for the front panel controls, Rl and R2, e.g., "Zero Adj" and "FS Adj"
  - e) Put the toggle switch in the up position with the push button switch pressed.
  - f) The panel meter should indicate the reading of the high-scale calibration reference. Record this reading.
  - g) If both references are checked perfectly, the operation and stability of the analyzer are verified.
  - h) If either, or both, of the reference checks are off by less than 1/2% of full scale (1/64 inch on the meter scale), no adjustment is required but optionally it may be performed if it is desired to trim up the calibration. This is accomplished by adjusting the

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front panel calibration controls, Rl and R2, to cause the analyzer to read the references exactly, as follows in (i), (j), and (k).

- With the push button pressed and the toggle switch down to read low-scale reference, adjust Rl until the panel meter indicates the low-scale reference exactly. Always adjust Rl first since it will effect both the low-scale and the high-scale readings equally. R2 will usually have a very small effect on the lowscale reading.
- j) With the push button pressed and the toggle switch up to read the high-scale reference, adjust R2 until the panel meter indicates the high-scale reference exactly.
- Repeat (i) and (j) as required until both references can be read exactly without further adjustment of either control.
- If the error noted in (h) is greater than 1/2% but less than 3%, follow the same adjustment procedure, but make a special note on the call report to watch the check of the analyzer on the next service call to see if a further shift of calibration occurs in the same direction.
- m) If the error noted (h) is greater than 3% of full scale, there is need for a troubleshooting check of the analyzer.
- 2) Perform the steps outlined in 1) to check the Temperature Analyzer.
  - a) The low-scale calibration reference is zero and the high-scale calibration reference is full scale.
- 3) Perform the steps outlined in 1) to check the Conductivity Analyzer.
  - a) The low-scale calibration reference is 1/6 of full scale and the high-scale calibration reference is full scale.
- 4) Perform the steps outlined in 1) to check the Dissolved Oxygen Analyzer.
  - a) The low-scale calibration reference is 1/6 of full scale and the high-scale calibration reference is full scale.
  - b) There is no R1 control on the dissclved oxygen analyzer.
- 5) Check the pH Analyzer as follows:
  - a) Open the lower analyzer cubicle drawer.
  - b) Remove the pH analyzer input coax cable from the connector on the rear left of the pH analyzer chassis deck. Replace it with the coax jumper and plug the pin on the jumper into the white test jack. This removes the pH glass electrode from the analyzer input and grounds the electrometer input without running the high-impedance circuit through the front panel switches.
  - c) Perform the steps outlined in 1)
  - d) The low-scale calibration reference is 7 and the high-scale calibration reference is full scale.
  - e) After check, or check and adjustment, remove the coax jumper and replace the input coax cable on the connector.

f) Close and fasten the lower analyzer cubicle drawer.

6) Perform the steps outlined in 1) to check the Solar Radiation Intensity Analyzer.

- a) The low-scale calibration reference is zero and the high-scale calibration reference is full scale.
- b) There is no R1 control on the solar radiation intensity analyzer.

7) Check the functioning of the telemeter transmitter by observing the transmission of a complete "line of data" in response to a call from the Central Station. This call may be a regular scheduled station call, or if more convenient, may be a manually-initiated call requested by telephone. Since the work at the monitor will usually require at least 45 minutes, it is quite probable that a regular station call will occur during the working time. This should be anticipated, and other activity suspended so that the transmission may be checked.

During the transmission, observe the performance of the oscillator by watching the blinking frequency indicator light and the telemeter line meter. With a bit of experience it will be possible to recognize the clean switching action which occurs when the oscillator is functioning properly as contrasted to the galloping blink resulting from trouble in the oscillator assembly.

Make a record on the service call report of the reading of each parameter as that parameter is being transmitted. Include the time of transmission, so that later this line of data can be compared to the line logged at the Central Station to confirm satisfactory transmisison.

Verification of the Dissolved Oxygen Reading

The importance of dissolved oxygen as a water quality parameter and the vulnerable nature of the dissolved oxygen electrode make it advisable to give this parametric system special attention during every service call. Care and patience are required to provide a validly calibrated and clean parametric system, but the extra care will be reflected in the data obtained.

1) After completion of the operation check for the dissolved oxygen analyzer and at least 5 minutes after the return of the dissolved oxygen sensor assembly to its flow cell, draw two water samples from that flow cell for Winkler titration.

2) Read and record the dissolved oxygen panel meter indication during the time that the BOD bottles are being filled. If there are slight fluctuations, try to record an average value. If any significant excursion in the reading (over 0.25 mg/l) occurs during this time, discard the samples and start over.

3) Prepare the samples and follow the Winkler titration procedure.

4) The average of the two titrations will be used as the titrated dis-

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solved oxygen value for comparison with the analyzer reading recorded in 2) above.

5) If this comparison is within 1% of full scale, (approximately 0.25 mg/1) the system should be considered properly calibrated and no adjustments should be made.

6) If the titrated dissolved oxygen value is higher or lower than the analyzer reading by more than 0.25 mg/l, but not more than 1.0 mg/l, merely adjust R2, the Full Scale Adjust control on the front sub-panel of the analyzer by an amount which will cause the analyzer reading to agree with the titrated value. Note that this adjustment should not make the present reading agree with the titrated value, the dissolved oxygen level in the water may have changed in the time elapsed during the titration. The amount of the adjustment should be determined by noting the percentage difference in values and adjusting the present analyzer reading by that percentage. For example:

DO indication when sample was drawn	= 7.0	) $mg/1$
DO concentration determined by titration	= 7.7	/ mg/1
Present DO indication	= 8.0	) mg/1
Required adjustment of indication =10% of 8.0	= +0.8	3 mg/1

7) If the difference between the titrated value and the analyzer reading is greater than 1.0 mg/l, additional factors concerning the electrode should be considered before making the decision to either adjust the analyzer or to replace the electrode. These factors are length of service, record of recent performance, and physical condition. Refer to the service log to determine the data of installation of the electrode and note the comparison between the titrated value of dissolved oxygen and the analyzer reading for the last two service calls. If the electrode has been in service longer than ten weeks, it should be replaced. If the period of use is less than ten weeks, but the recent service record indicates that the present discrepancy in reading is part of a developing trend (difference in the same direction and growing larger each week), the electrode should be replaced. There are other factors, some of which will be noticeable in a visual inspection, which will be cause for replacement of the electrode regardless of the past record.

8) If the electrode is not replaced, adjust R2 in the manner described in 5).

9) If the electrode is replaced, it will be necessary to allow at least one hour of operation of the replacement electrode before attempting adjustment of the dissolved oxygen parametric system. Then Steps 1) through 4) above should be repeated. After the titration is completed, R2 should be adjusted to cause the analyzer reading to agree with the titrated dissolved oxygen value as outlined in Step 6).

10) After any adjustment of R2 (whether or not the electrode has been replaced) it will be necessary to reset the calibration references by adjusting R4 and R5. Press the push button switch, put the toggle switch in and up position, and adjust R5 to cause the analyzer meter to read full

scale.

Check Out

1) Switch the telemeter transmitter test signal back to the normal 1000 level.

2) Close all drawers and doors and fasten them securly. All fasteners should be tightened; their purpose is to provide a compression of the gasket to seal the cubicles containing electronic equipment from dirt and moisture. Time saved by leaving the fasteners loose will be negligible compared to the time used working on the extra service problems which this practice may cause.

# Procedure for "Monthly" Calibration Checking and Preventive Maintenance

This procedure calls for all the work performed in the "weekly" cleaning and operation checking plus some additional cleaning of all parametric systems, and cleaning and lubrication of some of the system hardware.

Preliminary Steps

1) Perform Steps 1) through 6) of Initial Observation

2) Open the upper drawer of the analyzer cubicle and estimate the inside temperature; it should be about 105°F. Heaters, located on subpanels at the two sides of the cubicle are thermostatically controlled to maintain this temperature. If it is noticeably higher or lower, check the setting of the adjustable thermostat near the top on the right side.

3) A service light in the cubicle is switched by limit switches operated by the analyzer drawers. It should go on whenever an analyzer drawer is opened. Replace the bulb if it does not. CAUTION: Do not use a bulb of higher power rating than 40 watts; it may create a hot-spot problem for the nearest amplifier.

4) Inspect all analyzers to see that all plug-in components are seated properly in their sockets.

5) Check the analyzer cubicle front panels to see that each analyzer is securely fastened in its plug-in position to assure good contact at the Blue-Ribbion connector.

6) Perform Steps 1) through 7) of Cleaning.

7) For K=10 conductivity cells only, use the special spanner wrench provided to remove (turn CCW) the calibration plug ( see Dwg. #RM25-268). Clean the inside of the inner cup, the inside of the housing, and the plug, with wet tissue. Replace the plug by turning it clockwise until it seats on the shoulder. If the assembly is clean it will not be difficult to determine the end of travel. 8) Perform Steps 8) through 20) of Cleaning

9) Clean the solar radiation sensor by wiping the pyrheliometer bulb with a clean dry rag. Inspect for moisture condensation on the inside of the bulb.

10) Perform Steps 17 and 18 of Cleaning

11) Remove the end plug from the inlet reservoir, using the adapter plate provided for this purpose. This is a steel plate, approximately 2" x 3" x 1/8", which fits in the slot on the plug to permit removal of the plug with a small adjustable wrench. Use the plastic basin to catch any water that comes out of the reservoirs.

12) Clean the reservoir with the sponge mop. Open the flow valve briefly to flush the dirt into the basin. Replace the end plug.

13) Repeat 11) and 12) for the outlet header.

14) Inspect the effluent line and if necessary, clean it with the pipe auger using a rag wrapped around the tip of the auger.

15) Shut off the water flow at the service valve. Disconnect the inlet line from the monitor and run the pipe auger through the line. Open the service valve briefly to flush the line. Reconnect the line to the monitor and open the service valve. Experience may indicate that this cleaning operation need not be performed monthly; however, it must not be overlooked continually.

16) Open the flow control valve and adjust the flow to the proper rate.

- 17) After five minutes, review the parameter readings comparing them with the "after cleaning" readings previously recorded. Give special attention to the DO reading, since an increase may be an indication of inadequate initial flow. If there is a change, record it on the service call report as the DO reading "after flow adjustment." However, consider that some change in parameters of the water sample may have occurred in the stream during the time required for the cleaning.
- 18) If the initial observation of the flow conditions, or the change in DO reading after flow adjustment give cause to suspect a decrease in the incoming water supply since the last station visit, it may be advisable to check the supply line. In some cases, pebbles, small pieces of wood, etc., will accumulate in the line behind the service valve. Use of a mudleg will alleviate, but not completely eliminate this condition. Occasionally, it may be necessary to back flush the line or to remove the service valve for cleaning. A low flow situation must always be corrected promptly since it will create other problems if ignored.

19) Inspect the tops of the sensor assemblies and the flow cell terminal board to see that all leads are securely fastened.

20) If the flow cell terminal board is not entirely clean, it should be brushed carefully with a stiff-bristled brush (such as a toothbrush) to remove all dirt or salt. Wipe, as required, with a clean dry rag. Wipe the steatite standoff insulators with clean dry tissue.

21) Perform Steps 1) through 7) of Operation Checking

22) At this stage the parametric systems should be in good operational condition and ready for a calibration check.

Calibration Checking

This is a procedure for a simple calibration check of the complete parametric systems (sensors and analyzers) while they are in operation in the field. The primary purpose is to check the sensors, since the stability of the analyzers has already been cerified by the operation check against the built-in references. It is not as comprehensive as the initial, or basic calibration but is adequate to assure that system accuracy has been maintained.

The itemized procedure provides a guide line to accomplishing the work in a minimum elapsed time by checking all parametric systems simul-taneously.

It is presented for monitors having analyzers for temperature, conductivity, dissolved oxygen, pH, and solar radiation intensity.

1) All cleaning and operation checking has been completed in the steps outlined on page 8, Preliminary Steps.

2) The temperature parametric system will be checked at one point only, the present stream temperature.

3) Place the standard thermometer in the temperature/dissolved oxygen flow cell. CAUTION: Remember to remove the thermometer, to avoid breaking it, if the flow cell drawer is to be closed at any time.

4) The conductivity parametric system will be checked at a low-scale point approximately 1/6 of full scale, at mid-scale, and at full scale. This initial check, including a mid-scale point, will prevent the possibility of calibrating with badly contaminated standards or an unclean conductivity cell. If the initial check is satisfactory, calibration adjustments will be made using the low standard and the full-scale standard only.

For this procedure, it will be assumed that a 2400 micromho range is being checked, and that standard solutions of 2400, 1200, and 400 micromhos are available. NOTE: In the calibration of the conductivity parametric system, two portions of the same standard are employed. One is labeled a wash solution; the other, the primary standard. When a clean sensor is immersed into a wash, then into the primary standard of the same value, the droplets of solution remaining inside the sensor are of approximately the same conductivity as the primary standard and therefore will not contaminate it. Wash solutions should be discarded and replaced when they deviate by more than 10% from the standard solutions.

5) Remove the conductivity sensor assembly from its flow cell, shake it briskly to remove water from the vertical and horizontal bores, and dry it with tissue. Immerse the cell in the 400 micromho wash solution and swirl it to flush out the cell bores. Remove the assembly, shake it, dry it carefully, and insert it in the jar of 400 micromho standard solution. Put this test set-up aside for at least 5 minutes, to allow transients to subside, and proceed with the next step. NOTE: A low stool, bench, or table that can be placed beside the flow cell drawer will be convenient for location of standard solution jars during their test use.

6) The pH parametric system will be checked at a pH of 7 and a pH of 4 only. Calibration adjustments will be made using only these two buffers. The Fischer pH 7 buffer solution varies in pH from 7.0 at  $100^{\circ}$ F and  $77^{\circ}$ F to 7.1 at  $35^{\circ}$ F. The Fischer pH4 buffer can be considered to have a pH of 4.0 over the full temperature range.

Optionally, a high pH buffer (9 or 10) may be used for an additional check after calibration adjustment. However, these high pH buffers are of questionable value for field service. Each has a high temperature coefficient and the variation of pH with temperature is not linear. The pH10 buffer is much less stable than the 7 and 4 buffers. NOTE: Wash solutions are not required with the pH buffer solutions since the pH electrode assembly can be completely dried before being put into the buffer.

7) Remove the pH sensor assembly from its flow cell, dry it carefully, and insert it in the jar of pH7 buffer solution. Put this test set-up aside for at least 5 minutes and proceed with the next step.

8) Draw two water samples from the dissolved oxygen flow cell for Winkler titration. Read and record the dissolved oxygen panel meter indication during the time that the BOD bottles are being filled. If there are slight fluctuations, try to read an average value. If any significant excursion in the reading (over 0.25 mg/l) occurs during this time, discard the samples and start over. Add reagents and prepare the samples as instructed in Winkler procedure.

9) In the following, all transfers of sensor assemblies from one solution to another must follow the procedures outlined in the preceding steps.

10) Read and record on the service call report the conductivity analyzer panel meter indication for the 400 micromho standard solution.

11) Transfer the conductivity sensor assembly through the 1200 micromho wash solution to the 1200 micromho standard solution. Put this test setup aside for at least 5 minutes.

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- 12) Read and record on the service call report, the pH analyzer panel meter indication for the pH7 buffer solution. It is usually helpful to stir the buffer solution slightly with the electrode assembly about 30 seconds before taking the reading.
- 13) Remove the pH electrode assembly from the pH 7 buffer solution, dry it carefully with clean dry tissue, and insert it in the jar of pH4 buffer solution. Put this test set-up aside for at least 5 minutes.
- 14) Add acid to the two Winkler samples.

15) Read and record the conductivity analyzer reading for the 1200 micromho standard solution.

16) Transfer the conductivity sensor assembly through the 2400 micromho wash solution to the 2400 micromho standard solution. Put this test set-up aside for at least 5 minutes.

17) Titrate the two Winkler samples following procedure. If the results of the two titrations are within 0.25 mg/l of agreement, use the average of the two as the titrated dissolved oxygen concentration. If the results of the two titrations do not agree, it will be necessary to start over by drawing two new samples. Record the results of the titrations on the service call report.

18) Read and record the pH analyzer reading for the pH4 buffer solution.

19) Read and record the temperature indications of the standard thermometer and the temperature analyzer.

20) Read and record the conductivity analyzer reading for the 2400 micromho standard solution.

At this stage, a set of data will have been acquired covering the existing calibration of all of the parametric systems measuring water parameters. The calibration information will be useful in evaluating the stream data obtained by the monitor since the last calibration check.

The calibration information can be summarized as follows:

Parameter	Standard	Monitor
Temperature	Standard thermometer reading of sample water	Analyzer reading of sample water
Conductivity	400 micromho standard solution 1200 micromho standard solution 2400 micromho standard solution	Analyzer reading Analyzer reading Analyzer reading
рН	pH4 buffer solution pH7 buffer solution	Analyzer reading Analyzer reading

This comparison will determine if any parametric systems require calibration adjustment. A few general guide lines can be set up:

(a) Do not adjust calibration of a parametric system for which the analyzer readings are within 1/2% of agreement with the standards.

(b) If there is a difference of between 1/2% and 3%, adjust the calibration, note the adjustment on the service call report, and watch future calibration checks of the parametric system to see if a trend develops. Slow deterioration of a sensor may be detected in this manner.

(c) If a difference of 3% to 10% exists, look for the reason before changing calibration as a last resort.

(d) If a difference of more than 10% exists, the cause must be determined and the fault corrected.

For condition (c) or (d), the best aids for locating the trouble are: (a) the analyzer built-in reference check facility, (b) the service log, and (c) spare electrodes.

By referring to the service log, it can be determined whether any abnormal adjustments of the analyzer calibration controls, Rl and R2, have been made during the weekly operation checks since the last monthly calibration check. If not, and if the analyzer now checks the built-in calibration references (which were set immediately after the last calibration adjustment last month), then the analyzer must be in good order and is not a factor.

This means the "shift in calibration" is sensor oriented, that is, it is probably due to a change in the electrode, a defect in the temperature compensator, a poor connection in the sensor assembly wiring, or contaminated standard solutions or reagents. IMPORTANT: There is always the possibility that the present calibration check is valid, but that the previous calibration adjustment (last month) was bad due to poor standard solutions used then. A review of the service log will indicate whether any large changes were made in the other direction at that time.

The substitution of a spare electrode, known to be good, should always be one of the first measures used to further isolate the trouble. In most cases it will provide the solution.

Assuming that one or more parametric systems will require a calibration change for one reason or another the adjustment procedures in Steps 28) to 40) below should be followed. The precautions relating to drying of sensors, use of wash solutions, allowing 5 minutes response time, etc. will always apply but will not be repeated in the instructions for the individual steps.

21) To adjust the calibration of the temperature parametric system:

a) Read the present indication of the standard thermometer in the temperature/dissolved oxygen flow cell, and simultaneously read the temperature analyzer panel meter.

b) If the water temperature is below  $60^{\circ}F$ , use R1 to adjust the analyzer reading to agree with the standard thermometer reading. If the water temperature is above  $60^{\circ}F$ , use R2 for the adjustment.

22) To adjust the calibration of the dissolved oxygen parametric system: (a) Use the data already recorded as the basis for an adjustment of R2 as described in Step 6 of Verification of the Dissolved Oxygen Reading, Page 6.

23) To adjust the calibration of the conductivity or turbidity parametirc systems:

(a) Transfer the sensor assembly to the low-scale standard solution.

(b) Adjust Rl until the analyzer panel meter is correctly reading the low-scale standard solution.

(c) Transfer the sensor assembly to the full-scale standard solution.(d) Adjust R2 until the analyzer panel meter is correctly reading the full-scale standard solution.

(e) Return the sensor assembly to the low-scale standard solution. If the analyzer panel meter reading is exactly on for the low-scale standard, the calibration adjustment is completed. If not, then repeat Steps (b), (c), (d) and (a) in sequence, until both standard solutions can be measured correctly without further adjustment.

24) To adjust the calibration of the pH parametric system:

- (a) Transfer the pH sensor assembly to the pH7 buffer solution.
- (b) Adjust R1 until the pH analyzer panel meter reads 7.0.
- (c) Transfer the pH sensor assembly to the pH4 buffer solution.
- (d) Adjust R2 until the pH analyzer panel meter reads 4.0.

(e) Return the sensor assembly to the pH7 buffer solution. If the pH analyzer panel meter reading is 7.0, the calibration adjustment is completed. If not, then repeat Steps (b), (c), (d) and (a), in sequence until both buffer solutions can be measured correctly without further adjustment.

25) To adjust the calibration of the solar radiation intensity parametric system:

(a) The solar radiation intensity sensor is an Eppley Pyranometer which is a primary standard for this measurement; that is, it can only be checked against a second Pyranometer kept for that purpose and protected from damage and weather except when used for calibration checking.

(b) There is no reason to question the Pyranometer output unless the solor radiation intensity readings have been abnormally low over a long period of time despite sensor cleaning, or unless the visual inspection of Step 9) of Preliminary Steps, page 8, has revealed condensed moisture inside the glass bulb. If either condition occurs, and a replacement is not available, the Pyranometer may be returned to Eppley Laboratories for test.

(c) The calibration adjustment of the solar radiation intensity analyzer may be checked by measuring the potential at the gray jack at the top center of the analyzer chassis deck. This calibration reference potential should be 2.4 times the Pyranometer sensitivity in MV/calorie/ sq.cm./minute (marked for each Pyranometer on a metal tag on the base). The reference potential is usually 17 to 19 MV; the exact value for a particular sensor will be stamped on the chassis deck next to the gray jack. IMPORTANT: Pyranometers have different sensitivities and are not interchangeable in the parametric system without an adjustment of this reference potential. The potential at the gray jack is set by R5, the full-scale calibration reference control.

In the solar radiation intensity analyzer only, setting this reference R5, sets up the calibration also.

(d) After adjustment of R5 to give the correct potential at the gray jack, press the push button switch, put the toggle switch in the UP position, and adjust R2 (front sub-panel) to cause the analyzer panel meter to read full scale. NOTE: There are no R1 or R4 controls on this analyzer.

26) After calibration adjustment, if the settings of Rl and/or R2 have been changed for any analyzer, the references, R4 and R5, for that analyzer must be reset to correspond to the new calibration. NOTE: Adjustment of Rl or R2 constitutes a change in calibration.

Perform the following procedure for the temperature, conductivity, dissolved oxygen, and turbidity analyzers (not required for the solar radiation intensity analyzer):

a) Press the push button switch, put the toggle switch in the DOWN position, and adjust R4 (top rear left on the chassis deck) to cause the analyzer panel meter to read the low-scale reference marked on the front sub-panel (over control R1).

b) Press the push button switch, put the toggle switch in the UP position, and adjust R5 (top rear left on the chassis deck) to cause the analyzer panel meter to read full scale.

27) For the pH analyzer, follow the same procedure after removing the input coax from the connector, at top rear on the analyzer chassis deck, and replacing it with the coax jumper to ground (coax connector to white pin jack). Do not remove the jumper at this time.

Check the telemeter outputs for each analyzer as outlined in Step 28 below.

28) Check each analyzer telemeter output by measuring between the orange jack and the white jack at the front on the analyzer chassis deck. Use a digital voltmeter or MV potentiometer. With the push button switch pressed and the toggle swith up (panel meter reading an accurate full scale), the voltage should be 1000 MV; if it is not, adjust by turning R3B (top front center on the chassis deck).

29) Remove the coax jumper from the pH analyzer input connector and replace the input coax cable.

Preventive Maintenance

1) For the telemeter transmitter:

Perform the monthly program by cleaning the stepping switch the line relay and the recycling timer.

2) For the Flow Cell Drawer:

Wipe the drawer slides with a clean dry rag to remove dirt and dirty lubricant.

Lubricate with light oil applied in moderation to all segments of the slide assembly.

Lubricate the door latch mechanism with several drops of light oil.

There may be other service needs which will be noticed during work with the Robot Monitor. An effort should be made to take care of these requirements as they arise.

There are obvious benefits to be derived from keeping the insides of the cubicles clean and dry. Dust left in the cubicle will circulate and moisture can be harmful. The advantages in keeping the outside of the cabinet clean are largely aesthetic; but it is recommended that it be given enough attention to present an orderly appearance. A sloppy exterior appearance of instrumentation is often closely related to carelessness in other phases of its operation and maintenance.

## Checkout

1) Perform Steps 1) through 4) of paragraph on Checkout of page 8.

This procedure is subject to streamlining and some rearrangement may be desired based on experience, however, any short cuts devised must still accomplish the end results intended for the above routines, all parts of which are considered essential to attaining good performance.

## CHLORIDES\*

# Method of Calibration

The chlorides sensor assembly produces a millivolt output that varies as the negative logarithm of the chloride concentration with a potential offset, and varies with temperature. To calibrate, it is necessary to adjust the temperature compensation, to adjust the offset ("Zero Adj"), and to set the range ("FS Adj").

These operations require chloride standard solutions as follows:

- a) At 70°F; 1/6 of full scale approximately 1/2 scale full scale
- b) At 35°F; approximately 1/2 scale
- c) At 95°F; approximately 1/2 scale

Wash solutions are required for each of the three chloride values. The 1/2-scale solution will be used for temperature compensation and it is extremely important that all three portions of this solution be mixed together before each use. IMPORTANT: Chloride standard solutions should be handled with care and the jars should be capped at all times when the solutions are not in use; evaporation or condensation may cause a measureable change in a standard solution in several hours.

First, a preliminary calibration is performed at room temperature. The 1/6 adjust potentiometer, R1, which controls the offset, is adjusted to give the proper chloride reading for the low-scale standard solution when the sensor assembly is in that solution. The full scale adjust potentiometer, R2, is adjusted to give the proper chloride reading for the high-scale standard solution when the sensor assembly is in that solution. There will be some interaction between controls until the proper calibration is achieved. This will require several cycles through the two chloride solutions until each can be read correctly without any further adjustments. Anticipation of the interaction and suitable overadjustment may reduce the recycling required.

Temperature compensation is then performed with the mid-scale standard solution. R7 is used to adjust the reading when the sensor assembly is in the cold solution, R6 is used for adjustment at the high temperature and, R2 is trimmed as required to maintain the correct reading at room temperature.

After temperature compensation, the range adjustment will need

retrimming using R1 and R2 again, and looking at the low-scale and highscale standard solutions.

The characteristic compensation, to linearize the output, does not require separate adjustment; it is achieved by fixed components selected at time of initial factory calibration.

#### Recalibration Procedure

1) Preset all controls as follows:

a) If any new controls have been installed as an analyzer repair, adjust each to 12 turns clockwise by first turning 26 turns counterclockwise and then 12 turns clockwise.

b) If any controls have been turned far from their original adjustment by error or in an attempt to achieve a calibration with a defective sensor, reset them to 12 turns clockwise as in a).

c) Do not disturb any controls which retain their settings from the previous calibration; they are already at an optimum starting point.

2) Balance the 1556 amplifier output to 0.00V when the input is zero. (The amplifier balance control is RB next to the amplifier on the chassis deck). The 1556 output is measured between the green test jack and the rear white test jack. To achieve zero input, a) disconnect the chloride billet electrode lead from standoff insulator terminal III on the flow cell terminal board and jumper terminal III to ground, and b) disconnect the chloride reference electrode from the flow cell terminal board terminal #10 and jumper terminal #10 to ground. Do not reconnect the electrodes until Step 3) is completed.

3) Balance the P65AU amplifier output to 0.00V when the input is zero. (The amplifier balance control is recessed in the top of the amplifier housing). The output is measured between the blue test jack and either white test jack. To achieve zero input remove the 113 VAC input to the offset power supply by disconnecting the red/orange wire from the power panel terminal board terminal #9. Do not turn off "ANAL AC" switch since that would shut off the dual power supply. After completion of this step, restore all connections to operating condition.

4) Check the mechanical zero of the panel meter by removing the white/ orange lead from the panel meter "+" terminal. The meter must be at operating temperature. Adjust the mechanical zero set on the front panel of the meter as required. Reconnect the meter.

5) After all connections are restored, perform a preliminary range calibration using the 1/6 scale and full scale standard solutions. Adjust R1 when the sensor is in the 1/6 standard solution and adjust R2 when the sensor is in the full scale standard solution, following the procedure described above.

6) Temperature compensate using the 1/2 scale standard solutions at three temperatures; 35°F, 70°F, and 95°F, approximately. The standard solution jars placed in a container of crushed ice, at room temperature, and placed in a container of water on a thermostat-controlled hot plate, can be held at the required temperatures. Adjust R6, R7, and R2 as described Method of Calibration.

7) After the temperature compensation is satisfactory, perform a final range calibration using the low scale and full scale standard solutions at  $70^{\circ}$ F.

8) After the calibration is satisfactory, set the calibration references. Remove the input coax cable from the coax connector at the top rear left of the analyzer chassis deck. Replace it with the coax jumper and plug the pin on the jumper into the rear white test jack. With the push button switch pressed and the toggle switch down, adjust R4 to cause a 1/2 scale reading of the panel meter. With the push button switch pressed and the toggle switch up, adjust R5 to cause a full scale reading of the panel meter. Do not remove the jumper until Step 9) is completed. From: APHA Standard Methods, 13th ed. 97 (1971)

#### **PROCEDURE:**

- Take a water sample by filing a clean 100-ml graduated cylinder to the 100-ml mark. Pour the sample into a clean 250-ml Erlenmeyer flask.
- Add the contents of one Dipehnylcarbazone Indicator Buffer Powder Pillow and swirl to mix. (See Note A)
- Titrate the sample with Standard Mercuric Nitrate Solution, 0.0141N, while swirling flask until the color changes from yellow to a light pink. (See Note B)
- Multiply the number of ml of Standard Mercuric Nitrate Solution, 0.0141N, used by 5 to obtain the mg/l chloride(Cl).

## NOTES:

- A) The results will not be affected if a small portion of the Dipehnylcarbazone Indicator Buffer Powder does not dissolve.
- B) When the total amount of Standard Mercuric Nitrate Solution, 0.0141N, required exceeds 25 ml per titration, a sample dilution is recommended to minimize errors from multiple buret readings. The final results are then multiplied by the dilution factor.
- C) Chromate, ferric iron, and sulfite in excess of 10 mg/l interfere with this method. Sulfite interference can be eliminated by adding 3 drops of 30% hydrogen peroxide per 100 ml of water sample before running the test. Sulfide interference can be removed by adding the contents of one Sulfide Inhibitor Powder Pillow to: about 125 ml of the sample, mixing for one minute, and filtering through a folded filter paper. Iodide and bromide interfere directly and are titrated as chloride.

#### **REAGENTS:**

HACH Cat. No.Description285-16Standard Mercuric Nitrate, 0.0141N836-99Diphenylcarbazone Indicator Buffer Powder Pillows

# APPARATUS:

Buret, 25 ml Flask, Erlenmeyer, 250 ml Flask, Volumetric, 100 ml

# regulatory agencies of the signatory states

# ILLINOIS

Environmental Protection Agency State of Illinois 2200 Churchill Road Springfield, Illinois 62706 (217) 525-5467

# INDIANA

Indiana Stream Pollution Control Board 1330 West Michigan Street Indianapolis, Indiana 46206 (317) 633-4420

# KENTUCKY

Department of Natural Resources Capital Plaza Tower Frankfort, Kentucky 40601 (502) 564-3410

#### NEW YORK

Environmental Health Services NYS Department of Environmental Conservation 50 Wolf Road Albany, New York 12201 (518) 457-7362

# OHIO

Ohio Environmental Protection Agency P.O. Box 1049 Columbus, Ohio 43216 (614) 466-2390

# PENNSYLVANIA

Department of Environmental Resources P.O. Box 2351 Harrisburg, Pennsylvania 17120 (717) 787-2666

# VIRGINIA State Water Control Board P.O. Box 11143 Richmond, Virginia 23230 (804) 770-2241

# WEST VIRGINIA

Division of Water Resources Department of Natural Resources 1201 Greenbrier Street Charleston, West Virginia 25311 (304) 348-2107

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