# INVESTIGATION OF THE ORION RESEARCH AMMONIA MONITOR



Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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# INVESTIGATION OF THE ORION RESEARCH AMMONIA MONITOR

by

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ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY CINCINNATI, OHIO 45268

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#### FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati (EMSL) conducts research to:

Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments and solid waste.

Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water, and conduct studies to determine the responses of aquatic organisms to water quality.

Conduct an agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This report is part of a continued effort by the Instrumentation Development Branch, EMSL - Cincinnati, to investigate instruments and provide information to both users and suppliers. The intention is also to upgrade instrumentation and to make it possible to choose the most suitable instrument for a particular application.

Dwight G. Ballinger
Director
Environmental Monitoring and
Support Laboratory - Cincinnati

#### **ABSTRACT**

The Orion Research ammonia monitor was investigated using the Orion specifications and environmental considerations as a guide. Laboratory tests under controlled environmental conditions showed the electronic stability (drift) to be well within  $\pm 10$  percent of reading over the temperature range 5C to 42C. Sensor stability over the temperature range 5C to 42C was tested by applying ammonia nitrogen (standard solutions of 10 mg/l, 50 mg/l, and 100 mg/l) as direct input to the monitor. The results of these tests showed that automatic restandardization maintained readings within Orion's specified tolerance of  $\pm 10$  percent of reading.

Dynamic on-stream measurements were made of a secondary sewage treatment plant effluent in a field installation. These measurements were periodically compared with those of the standard method of distillation and titration. Sixty-five percent of these comparisons were within ±10 percent of reading. Steady-state comparisons were made of field-collected samples with the standard method for determining ammonia nitrogen. It appeared from these tests that a 5 percent loss in ammonia concentration resulted from the required straining and filtering of the sample input to the monitor. Eight of the nine samples compared were within 10 percent of the standard method.

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#### INTRODUCTION

#### AMMONIA LEVELS IN SEWAGE TREATMENT PLANT EFFLUENTS

Unpolluted surface waters contain relatively small amounts of ammonia and ammonium compounds. Higher levels than 0.1 mg/l ammonia nitrogen usually indicate organic pollution. A principle source of ammonia in surface waters is from treated wastes discharged from waste treatment plants. Domestic wastewaters are essentially urine, feces, and cellulose dispersed in relatively large volumes of water. Approximately 80 percent of the total nitrogen is introduced into wastewater as urea, which is rapidly converted to ammonia by the enzyme urease. The amount of nitrogen introduced into domestic waste is approximately 53 mg/l, of which 80 percent may be attributed to urea. Substantial variations from these values are encountered and are attributed to larger or smaller volumes of dilution water or additional sources of nitrogen.

Ammonia nitrogen discharged from waste treatment plants has several undesirable features<sup>3</sup>

- (1) ammonia consumes dissolved oxygen in the receiving water,
- (2) ammonia reacts with chlorine to form chloramines, which are less effective than free chlorine,
- (3) ammonia is toxic to fish life,
- (4) ammonia is corrosive to copper fittings, and
- (5) ammonia increases the chlorine demand at waterworks downstream.

Several methods have been developed to convert, reduce, or remove ammonia nitrogen from wastewaters. These include biological nitrification - denitrification, selective ion exchange, air stripping at elevated pH, and breakpoint chlorination. The characteristics of the wastewater, the extent of treatment, and the inclusion of one of the various ammonia removal techniques, then, results in a wide variability in ammonia levels discharged from waste treatment plants.

#### LABORATORY METHODS OF DETERMINING AMMONIA CONCENTRATION

Methods for Chemical Analysis of Water and Wastes<sup>4</sup> contains the analytical procedures used in U.S. Environmental Protection Agency (EPA) laboratories for the examination of ground and surface waters, domestic

and industrial waste effluents, and treatment process samples. Where economics and sample load do not warrant the use of automated equipment, the distillation procedure is the method of choice for determining ammonia nitrogen per liter (NH3 - N/1). The method is applicable in drinking, surface, saline, and domestic and industrial wastes. Samples are buffered with borate buffer and then distilled into a solution of The method covers the range 0.05 to 1.0 mg/1 NHz - N/1 for boric acid. nesslerization-colorimetric procedures, from 1.0 to 25 mg/l NHz - N/1 for the titrimetric procedure with standard sulfuric acid, and from 0.05 to 1400 mg/l NHz - N/l potentiometrically by the ammonia electrode. The ammonia selective electrode method is described for the range 0.03 to 1400 mg/l NH/z - N/l where distillation is not necessary. The automated colorimetric phenate method describes the determination of ammonia for the same type waters in the range 0.10 to 2.0 mg/1 NH<sub> $\chi$ </sub> - N/1. Higher concentrations can be determined by sample dilution. The Technicon AutoAnalyzer apparatus is used for this method.

Standard Methods requires preliminary distillation when interferences are present in determining ammonia nitrogen. Sensitivity is said to approximate 200  $\mu g/l$  NHz - N/l for direct nesslerization measurements. The phenate method is given tentative status and it lists a sensitivity for estimating ammonia of 10  $\mu g/l$  NHz - N/l and a usefulness up to 500  $\mu g/l$ . The titrimetric procedure, although subject to amine interferences, is said to be free of interferences from neutral organic compounds. The ASTM Standards lists methods of test for ammonia in industrial water and industrial wastewater. Two methods are described, the Referee Method (Distillation Method) and the Non-Referee Method (Direct Nesslerization Method).

#### PREVIOUS INVESTIGATION OF THE AMMONIA ELECTRODE

The Orion ammonia selective electrode was employed in the determination of ammonia in surface waters, sewage samples, and saline waters by Thomas and Booth. River and sewage samples were tested for ammonia by the electrode method and the indophenol blue method on a Technicon AutoAnalyzer and were found to be comparable. Advantages cited in the use of the ammonia electrode were minimal sample and reagent preparation prior to analysis, wide concentration range, precision and accuracy comparable to accepted methods, speed of determination, and moderate cost of the electrode.

LeBlanc and Sliwinski<sup>8</sup> analyzed biologically treated effluent samples, wastewaters from a food processing plant, an acid and explosive plant, a sulfite pulp mill, a kraft pulp and paper mill, and a chemical plant. Good correlation was obtained between the ammonia electrode method and by distillation with nesslerization and/or acid titration. Poor agreement, however, was obtained with untreated waste from the kraft mill. It was concluded that the ammonia electrode's good correlation with standard methods made it an excellent analytical tool for the measurement of ammonia nitrogen in wastewater.

Gilbert and Clay<sup>9</sup> evaluated the ammonia electrode on samples from different marine life display tanks and sea water samples. It was concluded the electrode provides an accurate means of analyzing ammonia in sea water and that it is usually more precise than the spectrophotometric method. Field analyses were equally favorable as those in the laboratory. Favorable results were also obtained by the ammonia electrode in sea water samples by Srna, et al.<sup>10</sup>

Orion has stated that monitoring systems can be designed for all laboratory methods of analysis utilizing ion-selective electrodes. The ammonia selective electrode is the focal point of an ammonia monitor developed by Orion Research. Physical and chemical pretreatment of a sampled stream enables continuous monitoring of the ammonia concentration. The monitor is designed for installation in an industrial environment with built-in capabilities for control. This report is the result of an investigation to evaluate the Orion Research Ammonia Monitor for its intended applications.

#### CONCLUSIONS

- 1. When a new or refurbished ammonia electrode is installed, a 16-hour transient drift occurs before equilibrium is established.
- 2. Although the lower decade slopes of three ammonia electrodes tested were somewhat less than the upper decade slopes, they were sufficiently close to warrant a 2-decade output range for the ammonia monitor.
- 3. The ammonia electrode's 90 percent of a decade change within 8 minutes appears to be adequate for the slowly changing ammonia concentration observed in a sewage treatment plant.
- 4. Electronic drift at constant temperature (20C) was less than 0.1 percent for a 3-day interval.
- 5. Electronic drift over the temperature range 5C to 42C averaged 1.8 mv per degree centigrade for a midscale setting. This drift did not exceed Orion's specified tolerance of ±10 percent of reading
- 6. Automatic restandardization restores sensor drift as a result of temperature change to within ±10 percent of reading over the temperature range 5C to 42C.
- 7. The steady-state performance of the ammonia monitor on a field sample was within ±10 percent of reading on eight of nine comparisons with a standard method. The samples were secondary effluent from a sewage treatment plant that were spiked over the range of the distillation and titration procedure for ammonia nitorgen.
- 8. The data from the laboratory test of a field sample suggest that a 5-percent loss of ammonia nitrogen occurs across the strainer and filter.
- 9. Dynamic on-stream measurements of ammonia of a secondary clarifier effluent were made with the ammonia monitor. Sixty-five percent of 23 sample sets analyzed with the standard method and the monitor were within ±10 percent of reading.

- 10. When tested at the 0.05 level of significance, there were no differences noted between the monitor data and data obtained by the standard method.
- 11. Improvement in the sample handling\* characteristics of the ammonia monitor would be desirable so that the introduction of solids would be less disruptive.
- 12. The tubing associated with the electrode holder of the constant temperature assembly (CTA) appears to be a chronic source of blockage problems.
- 13. The Orion ammonia monitor includes stable electronics that performed well under changing environmental conditions. The basic design of the monitor appears adequate for measuring ammonia nitrogen under changing environmental conditions and dissolved samples characteristics. Careful consideration, however, needs to be given to the sample intake to avoid excessive solids with the present sample handling. Care and attention, such as periodic backflushing of intake plumbing, is necessary to avoid clogging. The filter life, also, is reduced when excessive particulate matter is encountered. Interruptions in sample and reagent flow or filter breakthrough clog tubing within the CTA of the monitor. The present design requires complete replacement of the electrode holder when such clogging occurs.

<sup>\*</sup>Correspondence from Orion indicates an awareness of clogging problems and they have developed a Linear Membrane Filter (LMF) that eliminates 'breakthrough' and the resultant clogging of the monitor.

#### RECOMMENDATIONS

The Orion Research ammonia monitor performed adequately in the measurement of ammonia nitrogen where moderate amounts of particulate matter were encountered. Present monitor input sample handling requirements prevent its use in some locations where it is desirable to measure ammonia. Redesign or modification of sample input requirements, can extend the applicability of the ammonia monitor. Meanwhile, it is recommended that EPA place emphasis on research efforts to provide better sample conditioning for continuous monitors in general. Chopper pumps are available to reduce particle size of solids in liquids to 3.175 mm (1/8 in.). Further reduction of particle size is necessary. Present blenders are not manufactured to withstand the rigors of continuous operation. What is needed is rugged, dependable means of reducing particle size of solids in liquids. The small orifices and tubing requirements of reagent addition monitors are necessary for speed of response and to reach an economic compromise in reagent consumption. This being true, the particle size encountered must be controlled.

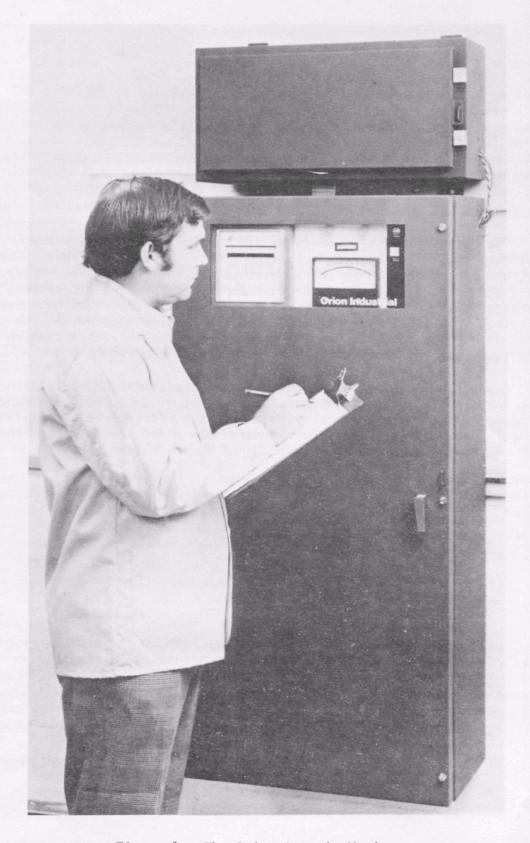


Figure 1. The Orion Ammonia Monitor

#### THE ORION AMMONIA MONITOR

#### MONITORS EMPLOYING GAS-SENSING ELECTRODES

The Orion Series 1000 monitors are continuous monitors which duplicate laboratory methods utilizing ion-selective electrodes. These monitors can be grouped in two general categories; those that employ solid-state electrodes and those that employ gas-sensing electrodes. Characteristics of monitors utilizing solid-state electrodes have been described in a previous report on the Orion Cyanide Monitor. <sup>11</sup> The model 1110 Orion Research ammonia monitor is equipped with a combination (internal reference electrode) gas-sensing electrode.

A paper by Ross, et al, $^{12}$  describes a theoretical model relating time response, electrical potential, and limit of detection as a function of membrane properties, geometry, and internal electrolyte composition for gas-sensing electrodes. Furthermore, the model predicts that the time response depends on the direction of concentration change:

$$t = \frac{1m}{Dk} \left[ 1.0 + \frac{dC_B}{dC} \right] \ln \frac{\Delta C}{\epsilon C_2}$$
 (1)

where 1 = thickness of internal electrolyte

m = thickness of membrane

D = membrane phase diffusion constant

k = partition coefficient of species between the aqueous sample, internal electrolyte phase, and the membrane phase

C = concentration of neutral species in internal electrolyte

 $C_{\rm R}$  = sum of concentration of all other forms, and

ΔC = concentration difference between inner and outer membrane interfaces

 $C_2$  = new equilibrium concentration of internal electrolyte

$$\varepsilon = \left| \frac{C_2 - C}{C_2} \right|$$

The combination electrode is composed of a fluorocarbon body with a hydrophobic, gas permeable membrane affixed with spacers at the tip. An epoxy inner electrode contains a flat pH glass electrode at the tip and a chloride ion electrode on the outer surface. A measured volume of internal electrolyte, ammonium chloride in solution with a nonaqueous additive, is introduced into the probe. The inner electrode is carefully placed within the probe, such that a small volume of internal filling solution is enclosed between the pH glass tip and a chloride ion electrode on the outer surface. A measured volume of internal electrolyte, ammonium chloride in solution with a non-aqueous additive, is introduced into the probe. The inner electrode is carefully placed within the probe, such that a small volume of internal filling solution is enclosed between the pH glass tip and the gas permeable membrane. The rest of the electrolyte forms a reservoir surrounding the inner electrode, in contact with the chloride ion electrode. The chloride ion electrode establishes a fixed, stable, reference potential with the high chloride ion in solution. small extent the ammonium chloride in solution forms the following equilibrium:

$$NH_3 + H_2O \Rightarrow NH_4^+ + OH^-$$
 (2)

Ammonia gas, penetrating the gas permeable membrane, shifts this reaction and a change in pH is detected by the glass electrode. The high concentration of  $\mathrm{NH_4}^+$  in the filling solution results in the  $\mathrm{OH^-}$  being directly proportional to the concentration of  $\mathrm{NH_3}$ . The measuring electrode potential may be described by:

$$E = S \log \left[ NH_3 \right]$$
 (3)

where

E = half-cell potential of the pH electrode

S = slope

$$[NH_3]$$
 = ammonia concentration

The half-cell potentials of the measuring and reference electrodes serve as input to a high-impedance-electrometer preamplifier in the electronics section of the monitor. A cross-sectional of the ammonia electrode is shown in Figure 2.

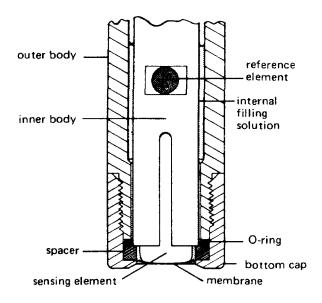


Figure 2. Ammonia electrode (courtesy of Orion Research Incorporated).

#### CHEMICAL SENSING PANEL

Sample handling within the monitor takes place on a fluid handling panel. Either sampling or standardizing solutions are selected by the operation of a valve controlled by circuitry within the electronics section. A proportioning pump feeds 1 ml per minute of sample and 0.22 per minute of reagent to a mixing chamber. A motor agitates two small magnetic stirrers to mix the sample/reagent as it is being fed to a constant temperature assembly (CTA). Air scrubbed of ammonia in a dilute acid solution is also pumped into the CTA. A block diagram of the fluids panel is shown in Figure 3.

An aluminum block in the CTA is machined to form the electrode holder and terminus for the fluids flow. The cool side of a thermoelectric cooler is butted up against the aluminum block under pressure. Heating elements and thermistor are imbedded within the block. The overall design is intended to maintain the electrode, with its internal components and filling solution, the aluminum-block-electrode holder, and the continuous flow of sample and air, all at a low temperature differential. A low operating temperature (18C-20C) is pursued in Orion's design so that water vapor (an interference at 28C and above) is reduced.

Tubing for the sample and airflow is coiled about the aluminum-block electrode holder and enters at a chamber in the lower end of the block. Here the sample tumbles down a ramp where the ammonia gas can escape into an air gap above. The airflow provides a continuous mixing so that rapid equilibrium is attained by the partial pressure of ammonia gas in contact with the electrode suspended from above. The electrode, therefore, is not in contact with the sample solution and, in fact, it is disruptive should this occur.

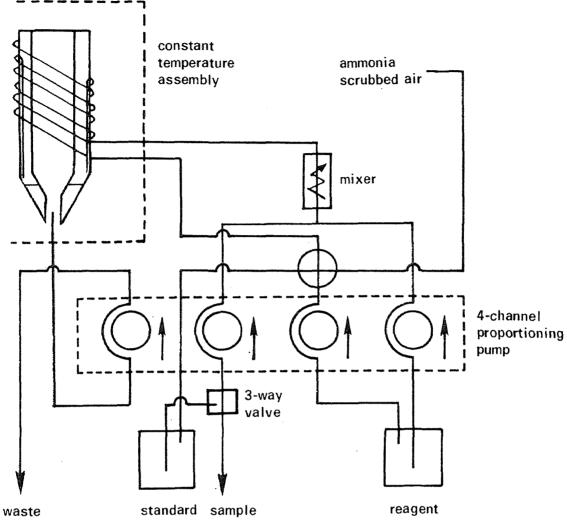


Figure 3. Fluids panel.

The reagent contains buffered EDTA that raises the pH of the sampled solution to 10.5. A sufficient fraction of gaseous ammonia exists at this pH and an economical compromise in reagent concentration is attained. Known gaseous interferences are mostly ionized at this high pH. Calcium and magnesium ions commonly encountered in sampled waters are complexed by the EDTA. If the osmotic pressure of the sample solution differs from that of the internal filling solution in the electrode, water vapor will diffuse across the membrane causing the concentration of ammonia inside the membrane to slowly change. A nonaqueous additive in the internal filling solution, and the osmotic strength adjustment of the reagent raise the osmotic pressure of each to an equally high and unchanging value.

The thermoelectric cooler is an interesting application of the Peltier Effect.  $^{13}$  It involves the heating or cooling of the junction of two thermoelectric semiconductor materials by passing current through the junction. A power supply with a low voltage, high current output passes a continuous current across the junction of an array of semiconductor

materials. The hot side is connected to a copper-block heat sink. A fan and a thin fin heat exchanger conduct the heat away. The cool side, as mentioned earlier is in contact with the aluminum block that forms the electrode holder. A thermistor imbedded in the block, in conjunction with a temperature control circuit in the electronics section, controls the on-off rate of the heating elements.

#### GENERAL CONSIDERATIONS

The intended usage of the Orion ammonia monitor is for fixed installation in an industrial location. Unless it is firmly mounted in a trailer, its overall design, physical dimensions, and weight rule out portability. The ammonia monitor is enclosed in a NEMA 12 case with overall dimensions of 167 cm high, 69 cm wide, by 36 cm deep (66 in. x 27 in. x 14 in.) and it has a mass of 145 kg (320 lbs). The input power may be selected from 100/115/220/240 VAC, 50/60 Hz, at 220 watts. A single reagent is supplied in a 3.785 liter (5 gal) container.

The purchase price of the Orion ammonia monitor is \$7,950. With continuous operation, there are sustaining reagent and supply costs. A service contract is available from Orion that provides replacements for reagents and for all expendable monitor supplies on a yearly basis for \$1,750. The replacement schedule is based on 1 year of continuous, 24-hour-per-day operation. For those who wish to operate intermittently, unit costs for items range approximately 20-30 percent greater.

#### LABORATORY INVESTIGATION

#### INVESTIGATION OBJECTIVES

Tests were conducted in the laboratory to investigate the performance capabilities of the Orion ammonia monitor. The objectives of these laboratory tests were to commence with the measurement of ammonia standards under favorable conditions, to continue under more difficult conditions and, eventually, to measure wastewater treatment plant effluent samples containing ammonia. Orion specifications and environmental considerations were used as a guide.

Monitor readings were compared with the ammonia of samples determined using analytical procedures from Manual of Methods for Chemical Analysis of Water and Wastes. Dr. Daniel F. Bender of the Physical and Chemical Methods Branch of EMSL performed these determinations at first and he later provided guidance to the author in determining the ammonia concentration of wastewater samples from a waste treatment plant effluent. Ammonia standards for most of the tests and all of the calibrations were derived from Orion 95-10-07 ammonia standard solutions. Large volume samples for long-term tests were prepared in-house.

Each individual test involved refurbishment of an ammonia electrode by changing the membrane and internal filling solution. This was done to avoid any possibility of there being undesirable characteristics to the electrode's performance as a result of idle periods between tests. The ammonia electrode was then installed in the monitor and operated overnight to reach complete equilibrium with an ammonia sample-input. Calibrations were performed the following day using the panel meter as the primary indicator. The zero and span controls of the Leeds and Northrup (L&N) recorder were also adjusted during calibrations for each test. Although Orion has indicated the greatest accuracy is attained by use of the panel meter, much of the data were derived from periods of unattended operation. Because of this, all data were extracted from the L&N strip chart. Difficulty was encountered in estimating values between the logarithmic chart marking of the L&N recorder. To eliminate guesswork, measured values were proportionately replaced on 8-1/2 by 10 inch, 2-cycle semilogarithmic graph paper.

#### AMMONIA ELECTRODE CHARACTERISTICS

The time interval required to reach chemical and thermal equilibrium for an installation of a refurbished ammonia electrode is illustrated in Figure 4. The resulting long-term transient requires that calibrations be made after a 16-hour interval. Certainly, calibrations cannot be made within a few short hours of electrode installation with any assurance of there being sufficient accuracy for important measurements or control. Approximate calibrations can be made within 3 hours but full calibrations should be made within 16 hours to assure maximum accuracy. All test data herein have been after calibration with at least 16 hours allowance to reach complete equilibrium.

Three electrodes were tested in the ammonia monitor with ammonia standards that covered the two logarithmic decade range of the instrument. The specified accuracy of the ammonia monitor is ±10 percent of reading and the lower-limit of detection is 1 ppm on the standard model (0.17 ppm with special scale and reagents). Each of the electrodes were installed, in turn, and the monitor was precalibrated with 10 mg/l and 100 mg/l standards. Standards ranging from 1 mg/l to 100 mg/l were applied as input to the monitor in, consecutively, decreasing and increasing concentrations. To establish uniformity and to assure complete electrode response readings were recorded from the strip chart 30 minutes after concentration changes. The longest response time, however, was encountered at the lowest-limit of detection (1.0 ppm). Therefore, these values were taken after 60 minutes; the results are illustrated in Table 1.

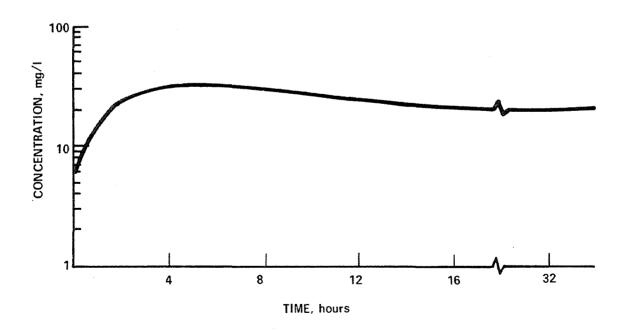


Figure 4. Ammonia electrode installation transient.

Table 1. TEST OVER COMPLETE OPERATING RANGE WITH AMMONIA STANDARDS

	Ammon	ia standard	s, mg/1 (de	ecreasing	conc.)
Electrode	100.0	50.0	10.0	5.0	1.0
Α	100.0	51.0	10.4	5.1	1.1
В	100.0	48.0	9.5	4.8	1.15
С	100.0	50.0	10.0	5.1	1.2
	Ammon	ia standard	s, mg/l (in	ncreasing	conc.)
	1.0	5.0	10.0	50.0	100.0
Α	1.1	5.0	10.2	51.0	100.0
В	1.15	4.6	9.5	49.0	95.0
С	1.2	5.0	10.0	51.0	99.0

The results of this test indicate that the instrument falls slightly short of being logarithmic over two full decades. With the exception of the 1 ppm lower-limit of detection, however, the performance of all of the electrodes were within Orion's specifications of ±10 percent of reading. Depending on the accuracies desired, the instrument should be calibrated over the decade of most interest. The error can be split between the extremes, for instance, by calibrating with 5 mg/1 and 50 mg/l standards.

Table 2 illustrates the results of a test to determine the slope, in millivolts per decade change of ammonia standards, for three separate ammonia electrodes. The ammonia electrodes were installed in the CTA of the monitor which maintained a 20C temperature. The proportioning pump applied standards, reagent, and airflow as usual. The electrode leads, however, were disconnected from the monitor and applied to a Keithley model 616, digital electrometer. A unity gain output from this instrument was measured by an Esterline Angus model S601S adjustable zero and span recorder. The results of this test indicate a difference in slope between the lower (1 - 10 mg/1) and upper (10 - 100 mg/1) decades. The percentage decrease in slope of the lower decade is listed for the respective electrodes in the  $\Delta$  percent column.

Table 2. SLOPE PER DECADE AT 20C, mv

	Ammo	nia decade change	, Δ mg/l
Electrode	1-10 mg/1	10-100 mg/1	Δ%
Α	51.2 mv	53.2 mv	4 decrease
В	49.5 mv	52.5 mv	6 decrease
С	49.5 mv	53.2 mv	7 decrease

Orion's specifications for response times are in terms of 90 percent of a decade change within 8 minutes. Preliminary tests in the laboratory have indicated response times within this interval. Without additional transit time of the sample through strainer, filter and related tube lengths, 90 percent response times between 5 and 6 minutes have been observed by three electrodes. The total response time is generally within 30 minutes. However, the decade change from 10 mg/l to 1 mg/l results in a total response time closer to 2 hours. Ross, et al, have derived a model for the time response (equation 1). Gilbert and Clay have also discussed the extended response times near the lower limit of detection, and have related them to leaching of ammonia from the internal filling solution reservoir. Nevertheless, one should be aware of the extended drift interval for the total response near the lower limit of detection.

#### ENVIRONMENTAL STABILITY

The ammonia monitor was installed in an environmental chamber. Shorting straps were inserted across the input to the preamplifier of the ammonia monitor and the slope and calibrate controls were adjusted for midscale deflection of the panel meter. This provided a suitable base signal for testing the electronic stability. The monitor was operated continuously under these conditions for 3 days with the environmental chamber controlled at 20C. A ±50 mv (zero midscale) recorder was placed on the preamplifier output (input to the L&N recorder). The drift range was a mere 3 mv during the 3-day interval. When related to the ±2.5 VDC output over the full scale range of the 2-logarithmic decade span of the ammonia monitor, the drift is less than 0.1 percent for the test interval. This small drift was not detectable on the less sensitive L&N recorder provided with the ammonia monitor.

The electronic stability was tested next over the temperature range 5C to 42C. The zero and span controls of the L&N recorder were adjusted at midscale and full scale. A midscale deflection was adjusted with the slope and calibrate controls. The environmental chamber's temperature was varied from the calibration temperatures of 20C over the 5C to 42C range. The recorded values from the 100 mv span auxiliary recorder and the output of the L&N recorder are listed in Table 3.

Table	3.	ELECTRONIC	STABILITY	WITH	TEMPERATURE

Temperature, C	Auxiliary Rcdr., mv	L&N Rcdr., ppm	Remarks
20	13	10.0	calibration
35	39	10.4	
42	52	10.6	
20	13	10.1	400 000
5	-14	9.9	

The values of Table 3 were taken after complete stabilization of temperature transients within several selected modules of the ammonia monitor. These temperatures were recorded once every 2 minutes from copper/constantan thermocouples. The maximum environmental chamber temperature selected adhered to Orion's specified operating limits. The drifts recorded by the L&N recorder were within Orion's specified accuracy of ±10 percent of reading. Although recorded values are with preamplifier input shorted, a thermocouple was placed within the CTA. An electrode was installed and fluids were pumped through the system so that temperature readings would approximate operating conditions. Overnight operation at each chamber temperature produced stabilization of the respective modules within the ammonia monitor, the results are illustrated in Table 4.

Table 4. MODULE TEMPERATURE AFTER STABILIZATION

Chamber temp.,	CTA temp., C	Monitor enclosure,	Electronics module C	L&N rcdr., C	Thermoelectric cooler power supply, C
20	15	26.5	29.5	35	39
35	19.5	39	42	49	53
42	24.5	48	51	57.5	58
20	15.5	27	30	39	39
5	14	11.5	13.5	22.5	24
20	15	26.5	29	36	38.5

The thermoelectric cooler and heating elements (CTA) maintained the temperature of the electrode-holder block within a range of 10C over the complete 37C temperature change (5C-42C). Thermal heat generated within the L§N recorder and the thermoelectric cooler power supply resulted in the highest temperatures recorded. Specifications for the L§N recorder restrict its operation to ambient temperatures of 50C. The maximum ambient temperature of 42C in this test was well within this restriction.

The operational stability of the overall system was tested at constant temperature in the environmental chamber. Calibration and restandardization solutions were derived from ammonia standards provided by Orion. A large volume (18 liter) sample was derived from stock solutions prepared by the Physical and Chemical Methods Branch. The concentration of this sample was 5.5 mg/l, and it was applied as input to the monitor for a 10-day interval. The environmental chamber was maintained at 20C; the results are illustrated in Table 5.

Table 5. SYSTEM STABILITY AT 20C

	L&N rcdr.,	Colorimetric determinations		overnight es, ppm	Restandardization,
Day	ppm	mg/l	Minimum	Maximum	μ amperes
	5.1	5.5	·	_	0
1	5.2	5.4	5.1	5.2	0
2	5.1	5.4	5.1	5.2	0
3	5.2	5.5	5.2	5.4	-1
4	5.1	5.4	5.1	5.1	-1
5		-	5.1	5.3	- -
6		<b>-</b>	5.1	5.3	<u>.</u>
7	5.1	5.6	5.0	5.2	-1
8	5.0	5.5	4.9	5.0	-1
9	5.4	5.5	5.1	5.5	0
10	5.4	<b>5.5</b>	5.2	5.4	-1

A sample removed each day was analyzed colorimetrically by nesslerization and spectrophotometric determination for ammonia nitrogen concentration. A comparison reading from the L&N recorder was taken at the same time. The minimum and maximum daily extremes were recorded in the intervening period, while discounting a 2-hour period for restandardization and the resultant transient response involved. During restandardization, 10 mg/l is applied to the monitor under the control of a timer. If a deviation from midscale is encountered, a servo motor automatically feeds back a signal to return the meter deflection to midscale. A restandardization meter measures the current in microamperes that results from these corrections. Nesslerization readings were consistently higher than the monitor readings, but the monitor was always within 10 percent. It is interesting to note that the lowest minimum and maximum values, listed on the eighth day, resulted in a correction that improved the accuracy of the monitor the following day.

The system stability was observed while varying the temperature of the environmental chamber over the range of 5C to 42C. The monitor was calibrated at 20C. Standards of 10, 50, and 100 mg/l were measured by the monitor at each temperature. A large volume sample (18 liters) was, again, derived from laboratory stock solution for continuous measurement. Colorimetric determinations of the sample were made after extreme temperature changes to assure that the ammonia concentration remained stable. The resulting data are illustrated in Table 6.

The minimum and maximum values indicate the overnight drift extremes during transients as a result of temperature changes. The L&N recorder column, however, were sample concentrations recorded after temperature stabilization and restandardization. The 10, 50, and 100 mg/l standards were also measured after stabilization. Estimates were made, where possible, for the 100 mg/l standard which deflected beyond full scale

Table 6. SYSTEM STABILITY OVER THE TEMPERATURE RANGE 5C TO 42C

extremes, ppm	Overnight	rcdr.	ards on LEA	Standa	Colorimetric determination	LGN rcdr.,		
Maximum	Minimum	100 mg/1	50 mg/l	10 mg/1	mg/l	ppm	Temp., C.	Day
-	-	100	52	10	6.0	5.6	20	-
5.6	5.0	-	-	-	-	5.4	5	1
5.5	5.4	-	-	-	-	5.3	5	2
5.3	5:2	F.S.(106)	53	9.9	-	5.4	5	3
-	-	F.S. (105)	52	9.8	5.8	5.5	20	-
5.3	5.0	F.S. (105)	53	9.7	-	5.3	35	4
6.0	5.1	F.S.	56	9.9	-	5.3	42	5
5.9	3.9	F.S. (104)	52	9.6	5.9	5.3	20	6

(F.S.) throughout most of the test. All of the other measurements, sample and standards, remained within 10 percent of their original values over the full 5C-42C temperature range.

#### FIELD SAMPLE MEASUREMENT

At this juncture, the ammonia monitor was prepared to accept samples characteristic of those encountered in the treatment of sewage. Orion supplies a filter panel that was mounted on the exterior of the monitor cabinet. Included are valves, a 0.22 micron millipore filter, and a 0-10 ml per minute sampling pump. The majority of the sample is by-passed across the face of the filter to waste. This continuously flushes particles away, preventing a build-up of materials that could clog the filter. A small volume (5 ml) of sample is pumped through the filter to a constant head chamber within the monitor cabinet. The life of the filter depends on the rate of flow past the outer surface of the filter element, thus, it is important that a pressure of 20-25 psi be maintained at the input.

The sample needs to be strained before entering the filter to prevent the passage of particles greater than 1/32 inch diameter. To accomplish this, Orion provided a reworked PVC "Y" strainer in a self-cleaning configuration. Self-cleaning takes place by returning 80 percent of the sample through a bypass in the strainer to waste. The strained sample (20%) is passed on as input to the filter panel. Figure 5 shows a cutaway of the PVC "Y" strainer.

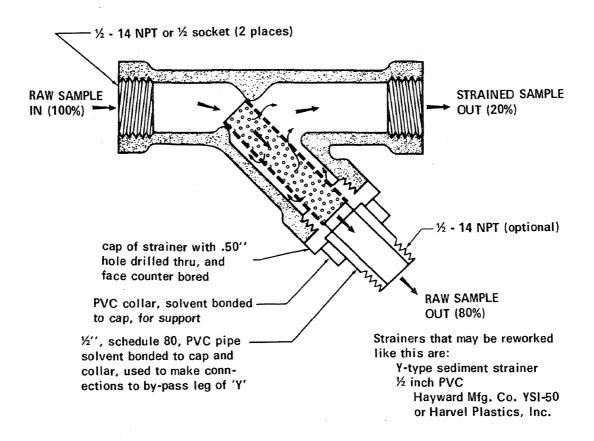


Figure 5. PVC "Y" strainer (courtesy of Orion Research Incorporated).

A pump was selected to continuously recirculate a sample. In the past, tests that required recirculating a sample were troublesome because pumps with suitable horsepower ratings to maintain Orion requirements of pressure and flow, imparted both an undesirable temperature rise and rust to the sample. Lower horsepower pumps with plastic and rubber materials, used as an alternative, were marginal in their ability to maintain suitable line pressures. A 1/2 hp Deming centrifugal pump with 3/4 inch pump discharge was instrumental in overcoming these problems. An extended shaft with a neoprene coupling reduced the temperature rise imparted from the motor. A corrosion resistant glass-reinforced, polyester casing and impeller eliminated the rust problem. The apparatus used for the test of a field sample is illustrated in Figure 6. Valve V<sub>3</sub> is throttled down to obtain the 20 - 25 psig on the pressure gauge.

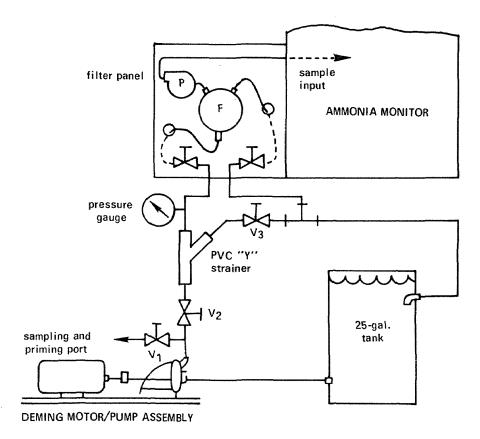


Figure 6. Field sample test apparatus.

A sample was collected, prior to chlorination from the secondary clarifier of the Muddy Creek Sewage Treatment Plant, Cincinnati, Ohio. Heavy rainfall the previous night resulted in infiltration, such that the ammonia concentration was below the 1 ppm lower limit of detection of the monitor. The purpose of this final laboratory test was to compare the readings of the ammonia monitor with those obtained by distillation and titration of the standard method. The effluent sample was recirculated through the 95 liter (25 gallon) tank shown in Figure 7. This was spiked with ammonium chloride to cover a range of values for the distillation/ titration procedure for  $NH_{3}$  - N/1. After equilibrium was reached with each spiking, samples were taken from within the tank, at the source, and after transit through strainer and filter. The ammonia concentration of these samples, determined by the standard method, represents the effect of straining and filtering under steady-state conditions. The corresponding monitor readings enable determining the accuracy of the ammonia monitor as a function of the standard method. The results are illustrated in Table 7.

Table 7. LABORATORY TEST WITH SECONDARY EFFLUENT WASTE FROM THE MUDDY CREEK WASTE TREATMENT PLANT

	on/titration, NH <sub>3</sub> -N/1			
source	filtered	Monitor response, mg/1 NH <sub>3</sub> -N/1	Percent source	Percent filtered
3.92	3.71	3.3	84	89
7.77	7.28	7.0	90	96
11.34	10.86	10.8	95	99
15.96	15.12	15.1	95	100
21.00	19.70	20.0	95	102
24.40	24.20	25.0	102	<u>103</u>
		Averages	93.5	98

The data of Table 7 indicates a favorable steady-state response of the ammonia monitor when compared with the standard method. All except the first comparison are within Orion's specifications of  $\pm 10$  percent of reading. The data also suggests there is a 5-percent loss of ammonia across the strainer and filter.

At this point, assistance from Dr. Bender was interrupted because he was obliged to prepare a paper. All subsequent chemical procedures were performed by the author with guidance from Dr. Bender. Another sample was obtained from the Muddy Creek Treatment plant and this time, naturally occurring ammonia was present. The sampling point was at the tank source. After determining the ammonia concentration the sample was spiked so that two more comparisons could be made. The results were similar to those of Table 7 and are illustrated in Table 8.

Table 8. ADDITIONAL SAMPLE FROM THE MUDDY CREEK WASTE TREATMENT PLANT

Distillation/titration mg/1 NH <sub>3</sub> - N/1	Monitor response mg/l NH3 - N/l	Percent source	Remarks
11.69	10.8	92	unspiked
16.45	15.2	92	spiked
22.05	20.0	91	spiked

#### FIELD INSTALLATION OF THE AMMONIA MONITOR

#### PRELIMINARY ARRANGEMENTS

Mr. Gerald G. Seymour, Assistant Superintendent of the Division of Operations, Metropolitan Sewer District, Cincinnati, Ohio, was most helpful in selecting a sewage treatment plant where the ammonia monitor could be installed. Two locations, each with secondary treatment, were visited. The Sycamore plant, employing contact stabilization, provided a readily accessible shelter for the monitor but it was remotely located insofar as sample pick-up was concerned. The Muddy Creek Sewage Works, an activated sludge plant, was selected because of convenience in sampling. Shelter for the ammonia monitor, however, needed to be provided at this location.

Shelter requirements were met by the National Field Investigation Center (NFIC) of EPA in Cincinnati, Ohio. Carl Hirth of NFIC obliged by providing a mobile van. The van installed at the Muddy Creek plant is shown in Figure 7. It is adjacent to a sewer located on the conduit from the secondary clarifier to the chlorine contact tank. The van serves as a mobile chemistry laboratory, and it includes an air conditioner, cabinet, sinks, refrigerators, intake and exhaust fans, and an electrical power panel. The electrical power panel services the aforementioned appliances and benchtop terminal strips. Many of these features were quite useful in conducting the field investigation of the ammonia monitor.

## SAMPLE INTAKE

Initially a 3/4 hp Jabsco pump was placed within the van, but its seal failed and another arrangement was pursued. A Jabsco model 12490-09, a totally enclosed 3/4 hp pump, was placed in operation outside the van. Figure 8 shows the suction line entering the grating access to the sewer. The output line feeds the monitor in the van. This arrangement worked successfully during the interval data were collected at this location. At the conclusion and prior to moving to the primary effluent, however, this pump also failed. Apparently, a particularly turbid sample was collected when the flow decreased such that the inlet strainer sank to bottom sediments. Figure 9 shows the intake removed from the sewer after this failure. A plastic strainer is shown attached to the end of the intake hose. The cylinder protruding is the inlet strainer for the ISCO sampler used for collecting samples for the laboratory analysis. Thus, the monitor and sampler intakes, as nearly as possible, represent the same sample.

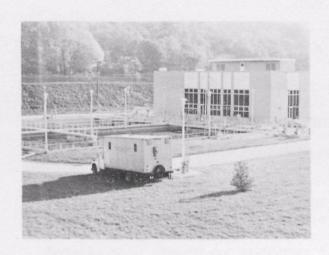


Figure 7. Mobile van installed at Muddy Creek Treatment Plant.



Figure 8. Intake pump installation.



Figure 9. Inlet strainer after test.

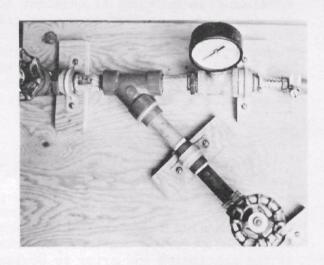


Figure 10. PVC "Y" strainer and associated components.

Figure 10 shows the PVC "Y" strainer and associated components on the inlet line to the monitor. Apparently, the by-pass valve (lower right of the photo) was the initial point of failure. Clogging of this valve with sludge from the bottom sediment resulted in a reduction in sample pumped. This resulted in the pump overheating, but prior to this the inlet pressure to the filter increased excessively, thus, rupturing it. The unfiltered sludge was pumped through to the 0.032 teflon tubing of the ammonia monitor, eventually clogging the tubing coiled about the CTA. Data were collected prior to this, however, to illustrate the performance of the monitor at this location. Plans to sample at the primary effluent were cancelled because of this failure.

#### SAMPLE COMPARISON

The purpose of this installation was to observe, on a short-term basis, the ability of the ammonia monitor to continuously measure the ammonia concentration of secondary sewage treatment effluent as compared to sampled values by the standard method of distillation and titration. As only a small number of comparison wastewater samples were analyzed at a single location, this is not intended as a complete and comprehensive investigation. It is, however, a demonstration of the ability of the ammonia monitor to perform the measurement of a wastewater effluent. In addition, following the recommended sample handling practices of Orion, it was intended to observe the performance under the expected variation in solids content of the samples encountered. In this respect Orion and future users may be aware of the pitfalls encountered.

Apparatus for four distillations were set up in the laboratory at 1014 Broadway, Cincinnati, Ohio. Samples were picked up at the treatment plant and transported to the laboratory each day. These samples were collected at timed intervals by an ISCO model 1391 water and wastewater sampler. At each 3-hour interval, a 500 ml sample was collected through the suction line strainer enclosed within the plastic-intake strainer previously described. The ISCO container was iced and sulfuric acid was added to each sample bottle to inhibit overnight changes in ammonia concentration. Table 9 lists the data collected for this test. Little difficulty in correlating the timed samples to the chart intervals of the monitor recording was encountered. This was because the changes in ammonia concentration recorded were gradual and over long intervals. Samples 2E and 4E were consecutive samples taken under nearly identical conditions. Sample 2E was determined the same day, whereas, sample 4E was iced overnight and determined the following day. Samples 1F and 3F were determined similarly. The preservation, therefore, did not result in a significant difference after overnight storage.

Table 9. COMPARISON OF AMMONIA MONITOR FIELD INSTALLATION DATA WITH LABORATORY ANALYSIS BY THE STANDARD METHOD

Sample number	Ammonia monitor, mg/l	Ammonia standard method, mg/l	Difference monitor - standard	$% = \frac{\text{Monitor}}{\text{standard}} \times 100$
4.6	2 7	1.0	0.4	121 0
4A	2.3	1.9	0.4	121.0
6A	3.1	2.3	0.8	134.8
8A	2.4	2.0	0.4	120.0
22B	7.5	8.3	-0.8	90.4
10C	5.1	4.7	0.4	108.5
11C	5.5	5.5	0.0	100.0
13C	4.6	4.8	-0.2	95.8
14C	3.6	4.2	-0.6	85.7
17C	7.4	7.1	0.3	104.2
20C	2.7	4.1	-1.4	65.8
12C	3.4	3.6	-0.2	94.4
13C	3.0	3.3	-0.3	90.9
1E	3.6	3.5	0.1	102.9
2E	3.6	3.4	0.2	105.9
4E	3.5	3.0	0.5	116.7
12E	9.2	9.0	0.2	102.2
13E	1.3	1.3	0.0	100.0
14E	7.8	7.5	0.3	104.0
19E	2.2	1.4	0.8	157.1
24E	2.0	1.6	0.4	125.0
26E	3.2	2.8	0.4	114.3
1F	2.3	2.2	0.1	104.6
3F	2.3	2.3	0.0	100.0
	•		1.8	2444.2

mean diff. = 0.08

mean % standard = 106.3

Assuming that the standard method is, indeed, superior to the ammonia monitor results, statistical methods  $^{14}$  were employed. The objective is to determine if there is a difference between the standard method and the monitor data of Table 8. Let  $\mu_M$  and  $\mu_S$  be the average ammonia concentration determined by the monitor and the standard method, respectively. Then the null hypothesis,  $H_0$ , is that  $\mu_M=\mu_S$ , or that their difference is zero. The alternative,  $H_1$ , is that  $\mu_M\neq\mu_S$ , or that their difference is not zero. Assuming the populations normal, and tested at the 0.05 level of significance, it was concluded that  $H_0$  could not be rejected. The two methods, therefore, were not seen to be significantly different.

A regression analysis was performed with the data of Table 8. The estimate of the regression line is illustrated in Figure 11 and is determined from comparison readings over the period of the test. The 95 percent confidence interval of the mean response is included. The standard deviation is 0.4919, with an estimated correlation coefficient of 0.974.

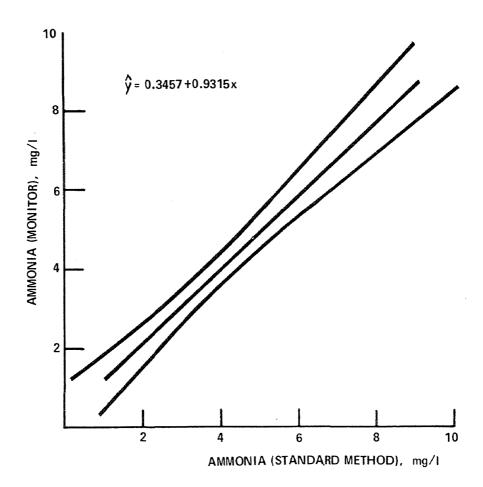


Figure 11. Regression line with 95 percent confidence limits for the mean response.

#### DISCUSSION

The field installation of the ammonia monitor accomplished the intended objectives of observing the monitor's performance as compared to sampling by the standard method and observing Orion's recommended technique in sample handling on the input. Figure 12 shows that 65 percent of the monitor readings were within  $\pm 10$  percent of the standard method values.

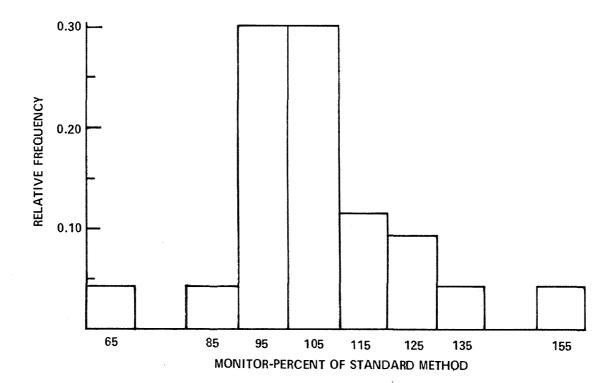


Figure 12. Relative frequency histogram.

Improvement would be desirable in the sample handling requirements of the ammonia monitor. During the interval in which data were collected, heavy flow and moderate amounts of solids were encountered. Weekly backflushing of the by-pass strainer resulted in successful operation. Later a reduced flow caused a lowering of the intake such that bottom sludge was pumped. This resulted in clogging of the by-pass valve, rupture of the filter, and failure of the pump. The sludge was passed on into the small diameter tubing within the monitor, eventually clogging it. Present requirements to throttle down the by-pass valve (to obtain 20 - 25 psi on pressure gauge) results in a small bore opening in the valve to waste. This small opening is vulnerable to clogging and it requires periodic flushing and the avoidance of excessive solids at the intake. With the present sample handling, intake placement must be planned carefully to reduce the likelihood of pumping solids. Preventive maintenance requires that the strainer be back-flushed as often as necessary depending on the sample characteristics.

A problem area within the ammonia monitor, warranting examination by Orion, is the transport of liquid-sample/reagent through the coiled tubing about the electrode holder. Blockage can presently occur from failures resulting in solids breakthrough into the monitor or in interruptions of the normal flow of liquids. In either case, solidification can occur within the tubing. When these blockages do occur, the complete electrode holder assembly needs to be replaced. A redesign or modification, possibly taking advantage of the electrode's measurement of ammonia in the gaseous state, would be desirable. That is, Orion might consider the transport of gaseous ammonia, rather than liquids, through the tubing into the CTA.

#### REFERENCES

- 1. Zadorojny, C., S. Saxton, and R. Finger. Spectrophotometric Determination of Ammonia. JWPCF, 45, 5, p. 905, May 1973.
- 2. Hanson, A. M. and G. F. Lee. Forms of Organic Nitrogen in Domestic Wastewater. JWPCF, 43, 11, p. 2271, November 1971.
- 3. Barth E. F., and R. B. Dean. Nitrogen Removal from Wastewaters. In: Proceedings of Advanced Waste Treatment Water Reuse Symposium, Environmental Protection Agency, Washington, D.C., 1971.
- 4. Manual of Methods for Chemical Analysis of Water and Wastes. Technology Transfer, p. 159, STORET NO. 00610, U.S. Environmental Protection Agency, Washington, D.C., 1974.
- 5. American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 222, Method 132, New York, 1971.
- 6. ASTM Standard, Part 23, Water; Atmospheric Analysis, p. 368, Method D1426-58, 1973.
- 7. Thomas, R. F., and R. L. Booth. Selective Electrode Measurement of Ammonia in Water and Wastes. Environmental Science and Technology, Vol. 7, p. 523, June 1973.
- 8. LeBlanc, P. J., and J. F. Sliwinski. Specific Ion Electrode Analysis of Ammonium Nitrogen in Waste Waters. American Laboratory, Vol. 5, No. 7, p. 51, July 1973.
- 9. Gilbert, R. R., and A. M. Clay. Determination of Ammonia in Aquaria and in Sea Water Using the Ammonia Electrode. Analytical Chemistry, Vol. 45, No. 9, p. 1757, August 1973.
- Srna, R. F., C. Epifanio, M. Hartman, G. Pruder, and A. Stubbs. The Use of Ion Specific Electrodes for Chemical Monitoring of Marine Systems. College of Marine Studies, University of Delaware (DEL-SG-14-73), June 1973.
- 11. O'Herron, R. J. Investigation of the Orion Research Cyanide Monitor. EPA 670/4-75-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1975.

- 12. Ross, J. W., J. H. Riseman, and J. A. Krueger. Potentiometric Gas Sensing Electrodes. Pure and Applied Chemistry, Vol. 36, p. 473, 1973.
- 13. Benner, P. E. Direct-Energy Conversion. Standard Handbook for Mechanical Engineers, Baumeister and Marks, Editors, 7th Edition, McGraw-Hill, New York, 1967.
- 14. Walpole, R. E. and R. H. Myers. Probability and Statistics for Engineers and Scientists. The Macmillian Company, New York, 1972.

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# 15. SUPPLEMENTARY NOTES

#### 16. ABSTRACT

The Orion Research ammonia monitor was investigated using the Orion specifications and environmental considerations as a guide. Laboratory tests under controlled environmental conditions showed the electronic stability (drift) to be well within  $\pm 10$  percent of reading over the temperature range 5C to 42C. Sensor stability over the temperature range 5C to 42C was tested by applying ammonia nitrogen (standard solutions of 10 mg/l, 50 mg/l, and 100 mg/l) as direct input to the monitor. The results of these tests showed that automatic restandardization maintained readings within Orion's specified tolerance of  $\pm 10$  percent of reading.

Dynamic on-stream measurements were made of a secondary sewage treatment plant effluent in a field installation. These measurements were periodically compared with those of the standard method of distillation and titration. Sixty-five percent of these comparisons were within ±10 percent of reading. Steady-state comparisons were made of field-collected samples with the standard method for determining ammonia nitrogen. It appeared from these tests that a 5 percent loss in ammonia concentration resulted from the required straining and filtering of the sample input to the monitor. Eight of the nine samples compared were within 10 percent of the standard method.

17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS	b.IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Ammino compounds, Ammonia, Electrodes, Test chambers, Environmental tests, Measuring instruments, Monitors, Performance evaluation, pH, Samples, Sewage treatment, Specifications, Waste treatment	Gas-sensing electrodes, Industrial effluent, Osmotic strength, rea- gent additions, Suspended solids, Total concentration	13B	
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