

EPA-670/4-75-005
April 1975

Environmental Monitoring Series

INVESTIGATION OF THE ORION RESEARCH CYANIDE MONITOR



National Environmental Research Center
Office of Research and Development
U.S. Environmental Protection Agency
Washington, D.C. 20460
45268

EC-1

EPA-670/4-75-005
April 1975

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By

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Program Element No. 1HA327

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U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides; radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multi-disciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This report is part of a continued effort by the Instrumentation Development Branch, Methods Development and Quality Assurance Research Laboratory (MDQARL), NERC-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.

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ABSTRACT

The model 1206 Orion Research cyanide monitor was investigated using the Orion specifications and environmental considerations as a guide. This is one of the Series 1000 monitors manufactured by Orion which duplicate laboratory analyses made with ion-selective electrodes. The Series 1000 monitors perform single parameter measurements of concentration, it is reported, and continuously display the results on a panel meter and a strip chart recorder. Sample pretreatment techniques are applied against an array of interferences encountered in the use of ion-selective electrodes. The cyanide monitor employs a silver/sulfide--sodium reference electrode set in the indicator method to detect, continuously, the level of cyanide in a sampled stream. Cadmium, copper, nickel, and zinc complexes of cyanide are broken by two reagents added in the fluids-chemical section. The breakdown of tightly bound cyanide complexes of iron, cobalt, and platinum are not effected by the addition of these reagents. Hydrogen cyanide (HCN) is converted to the free cyanide ion for detection by the electrodes.

Laboratory tests under controlled environmental conditions showed the electronic stability (drift) to be within 0.1% over the temperature range of 5C to 35C. Sensor stability, over the temperature range 5C to 35C was tested by applying free cyanide ion (standard solutions of 1 mg/l and 10 mg/l) as direct input to the monitors. The results of these tests showed that Orion's specified tolerance of $\pm 10\%$ of reading was met. Two out of three electrode sets tested for linearity were within Orion's tolerance of ± 0.02 ppm below 0.25 ppm and $\pm 10\%$ of readings above 0.25 ppm cyanide concentration.

Dynamic on-stream measurements were made from a metal plating process rinse stream in a field installation of the monitor, and these measurements were periodically compared with those of the standard method for total cyanide. This field installation revealed the comparisons were widely variable. Steady-state comparisons were made of field-collected samples with the standard method for determining total cyanide. These tests revealed that a 15% to 20% loss in cyanide concentration resulted from the required straining and filtering of the sample input to the monitor.

CONTENTS

	<u>Page</u>
Abstract	iv
List of Figures and Tables	v
Acknowledgments	vi
Sections	
I Conclusions	1
II Recommendations	4
III Introduction	5
IV The Orion Cyanide Monitor	8
V Laboratory Evaluation	11
VI Field Evaluation	17
VII Laboratory Tests with Field Sample	22
VIII References	24

FIGURES AND TABLES

Figure Number

1	Series 1000 Monitors	8
2	Block Diagram of the Chemical Sensing Section	10
3	Preamplifier Output Voltage--CTA Temperature Transition from 45C to 30C	14
4	Fluid Connections to Monitor	17
5	Regression Line with 95% Confidence Limits for the Mean Response	21

Table Number

1	Ten Day Operation	11
2	Environmental Tests with Continuous Measurement of Sample	13
3	Linearity and Lower Limit Detection of Cyanide Standards	15
4	Comparison of Cyanide Monitor Field Installation Data with Laboratory Analysis of Total Cyanide	20
5	Relative System Response with Varying Pressure Input	22
6	Laboratory Test with Cyanide Waste Samples Col- lected in the Field	23

ACKNOWLEDGMENTS

We gratefully acknowledge the support and help of L. B. Lobring (Physical and Chemical Methods Branch, MDQARL) in preparing standards and analyzing samples; P. P. Kovatis (of the Metal Finishers Foundation) in securing industry cooperation to permit the monitor to be installed on a cyanide waste stream; R. P. Lauch (Instrumentation Development Branch, MDQARL) for contributing suggestions that helped in selecting hydraulic test apparatus; and T. J. Stasiak and W. T. O'Connell (Orion representatives) for their installation assistance and helpful suggestions throughout this investigation.

SECTION I

CONCLUSIONS

1. Modification in components and procedures made by Orion during the interval of this evaluation of the cyanide monitor indicated the model tested was still in the prototype stage of development.
2. Being in an early stage of production, some improvements in quality control of components appear to be necessary.
3. Electronic drift at constant temperature (20C) was less than 0.1% for a 1-week interval.
4. Electronic drift over the temperature range 5C to 35C was 0.12%.
5. Sensor drift over the temperature range 5C to 35C was within Orion's specified tolerance of $\pm 10\%$ of reading for cyanide standards of 1 mg/l and 10 mg/l. This occurs if the operation is within Orion's framework: the constant temperature assembly is maintained 5C above ambient temperatures of 25C and the automatic restandardization has taken place after the temperature change.
6. Two of three electrode sets tested were within Orion's tolerance of ± 0.02 ppm on concentrations below 0.25 ppm cyanide and $\pm 10\%$ of reading on concentrations above 0.25 ppm cyanide. The other electrode set ranged slightly higher--to within 0.04 ppm on concentrations below 0.25 ppm cyanide.
7. As a result of this investigation, Orion has had the instruction manual, which lacked clarity and depth, rewritten and broadened in scope.
8. Data from the cyanide monitor installed in a field location varied widely from the standard method determinations of total cyanide. This variability was caused by:
 - a. an inability to maintain input pressure to the filter at the recommended 15 to 20 psi: the strainer and a throttling valve clogged when the monitor was unattended,

- b. a drop in cyanide concentration across the strainer and filter,
 - c. an inability of the monitor to measure total cyanide, and
 - d. the long delay (8 to 10 minutes with adequate pressure input) of fluids in transit and of electrode response dampened the abrupt and cyclic variations in cyanide concentrations of the wastewater sampled. (Note: Discussions with Orion personnel about problems encountered in maintaining suitable pressure input to the filter has resulted in a new prefilter design.)
9. Steady-state tests with field samples showed that a 15% to 20% loss in cyanide concentration occurred across the strainer and filter.
10. Essentially all of the cyanide passing the filter was measured by the monitor for these particular samples. (Note: This is sample dependent.)
11. Response time to a change in cyanide concentration was a function of the sample input pressure.
12. As a result of the number of tests and the length of time necessary to complete these tests, there were no long-term tests made of the effectiveness of either the electrodes (4 month replacement) or the filter (1 month replacement).
13. The monitor does not measure iron, cobalt, platinum, gold, and silver complexes of cyanide. Chlorine is a negative interference. High levels of sulfide (10 mg/l and above) cause a positive interference and must be avoided. Orion continues its research effort to counteract these interferences.
14. In summary, the cyanide monitor includes stable electronics that performed very well over changing environmental conditions. Ambient temperature should be controlled, not to exceed 30C because high temperature reduces the life of the electrodes. Fluids flow requires that the temperature be controlled above 0C. The reference voltage feedback technique employed in the automatic restandardization approach is clever; it is effective in compensating for the long-term drift that's encountered in the use of ion-selective electrodes. Application of the monitor should not be considered

routine. Care and maintenance will be a continuing requirement. Qualified personnel, aware of sample characteristics and monitor limitations, are required to interpret the data; i.e., qualified chemists should perform periodic comparison tests with the standard method for total cyanide. The monitor measures some of the loosely bound metal cyanide complexes, but not those which are tightly bound. The presence and the effect of other interferences, e.g., chlorine and sulfide, on the electrode signal output should be known.

SECTION II

RECOMMENDATIONS

The Orion cyanide monitor does not measure total cyanide, and problems were encountered with its use. However, the standard method for measuring total cyanide cannot be performed rapidly, unattended, inexpensively, continuously, or with few problems. Each method performs capably in some category. Therefore, it is recommended that the desirable qualities of each be utilized to their fullest extent. The cyanide monitor cannot measure total cyanide, but with care and proper maintenance, it can measure some forms of the cyanide present in certain wastes. And Orion is planning future improvements. At present, the cyanide monitor can be used where continuous surveillance is required on wastes suspected of having excessive cyanide. Dual set-point, high- and low-alarm limits, included in the monitor, can be employed to actuate a sampling device when a predetermined limit has been exceeded. Thus, samples can be screened in the field so that the time-consuming analysis of the standard method for total cyanide can be expedited. If it can be shown that positive interferences are not present, gross violations of effluent standards as indicated by a calibrated and functional monitor, should be useful.

The Orion Series 1000 monitors are designed and developed to meet needs of Industry. As a result of these developments, as in the case of the cyanide monitor, these instruments could also be of use to EPA procurements provided the application and performance requirements are well defined.

SECTION III

INTRODUCTION

Ion-selective electrodes developed within the past two decades have been employed with instrument systems under favorable process conditions for control purposes. Generally, these instruments were utilized as indicators of gross process upsets. The mere presence of a measured parameter could be indicative of a breakdown at some point within a process. In these earlier process control applications of ion-selective electrodes, pretreatment of the sample has primarily involved obtaining favorable pH and controlling the temperature. These instrument systems measured sample parameters under favorable process conditions and performed useful control functions in industrial processes. That is, the uncomplexed, free ion was measured in samples where interferences were known to be minimal.

In recent years, several manufacturers have made a concerted effort to use continuous monitors for concentration values of parameters. Interferences encountered with the use of ion-selective electrodes make it necessary to pretreat the sample in monitoring systems. The interferences can be due to the sample itself or to the measuring electrode and the reference electrode. Ion-selective electrodes respond to the free, unbound ion, not the total concentration of a chemical species. Increased use of ion-selective electrodes in laboratory analyses over the years has resulted in methods being developed to free bound ions so that concentrations can be determined. Ions resulting in electrode interferences must be either removed or avoided through chemical pretreatment techniques. The amount and type of other ions in solution (ionic strength)¹ affect the signal output of ion-selective electrodes. The activity, a , of an ion is related to the concentration, C , by the equation

$$a = \gamma C \quad (1)$$

where γ is the activity coefficient, which is dependent upon the total ionic strength of the solution. Ionic strength adjusters (ISA) are available that when added to standardizing solutions and samples, "swamp out" differences so that the activity coefficient of the ion being sensed is about the same in all solutions.

The pH of the sample may also result in interferences: bound ions

may be decomplexed at a favorable pH or interfering ions may be preferentially complexed within a certain pH range. In addition, either the hydrogen (H^+) or hydroxyl (OH^-) ions may be an electrode interference. Therefore, sample pH adjustment is a usual requirement.

The voltage output of ion-selective electrodes is characterized by the Nernst equation at constant temperature.

$$E = E^\circ + (0.19841T/n) \log a_i \quad (2)$$

The variation as a result of temperature change is described by T. S. Light.²

$$\begin{aligned} dE/dT = dE^\circ/dT + (0.19841/n) \log a_i + \\ (0.19841T/n)(d \log a_i/dT) \end{aligned} \quad (3)$$

Sample temperature affects not only the Nernstian slope term $[(0.19841/n) \log a_i]$, but also the "solution temperature coefficient" term $[0.19841T/n)(d \log a_i/dT)]$. Light has discussed the solution temperature coefficient term:

"The activity of an ion may be affected by its activity coefficient and for weak or complex forming electrolytes by its equilibrium relationships. Since activity coefficients and equilibrium constants may each have temperature coefficients of their own, the 'solution temperature coefficient' term may become quite complex."

Because temperature compensation techniques normally correct for the Nernst slope term only, temperature control of the sample is generally selected by Orion. Sample color and turbidity do not interfere with the voltage relationships in the use of ion-selective electrodes. Filtering is necessary, however, to combat clogging of tubing or fouling of electrodes.

In regard to reference electrodes, Orion has stated, "Our experience over the past several years has shown that most of the problems that users of specific ion electrodes have reported to us are directly traceable to the liquid junction in the external reference electrode."³ Requirements for 0.1 to 0.2 mv accuracy

for 1% to 2% ion activity, as opposed to approximately 6 mv to obtain 0.1 pH unit accuracy, were indicated. These tougher requirements for specific ions have led Orion to advise using a second specific ion electrode,⁴ as a reference electrode--one whose level can be kept constant.

