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EVALUATION OF THE RING OVEN TECHNIQUE FOR WATER MONITORING.(U)

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# EVALUATION OF THE RING OVEN TECHNIQUE FOR WATER MONITORING.

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Alexandria, Virginia 22314

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*
Ring oven tests for ten ions that had been developed under another contract (DADA17-73-C-3112) were subjected to statistical testing to determine the procedures' accuracy, precision, operator variability, and the effects of variable factors found in the environment. Procedures for six of the ten ions (copper, calcium, magnesium, zinc, chloride and sulfate) were found to be suitable for screening of natural waters; those for nitrates, fluorides, lead and iron were not suitable. Feasibility studies were also performed for ring oven techniques for the determination of pesticides in water and for general scan purposes.

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# EVALUATION OF THE RING OVEN
# TECHNIQUE FOR WATER MONITORING

FINAL REPORT

October 1977

By

Roger E. Snyder
Martha E. Tonkin
Alton M. McKissick
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# EXECUTIVE SUMMARY

The objective of this research study, performed under Contract No. DAMD17-76-C-6049, was a comprehensive statistical evaluation of ring oven/spot test procedures developed for the field monitoring of natural waters. These procedures were previously developed under Army Contract No. DADA17-73-C-3112, and consisted of ring oven tests for the ions copper, calcium, magnesium, zinc, iron, lead, nitrate, fluoride, chloride, and sulfate. Statistical test matrices were designed in a manner that permitted the accuracy, precision, operator variability and the effect of environmental variables on the ring oven procedure to be ascertained.

Permanent standard rings were prepared during this contract effort. Several methods for the preparation were investigated, including color photography and four-color printing. The method of choice for the standards was the dye transfer process, which was used to manufacture permanent standards for eight of the ten ions investigated. These standards were then used for the statistical qualifications testing.

Fractional factorial testing was performed for the ten ions, using a half-replicate design. This testing was designed to show the effects of varying certain factors that can change with environmental conditions. Synthetic water samples were prepared to simulate the factors being tested in order to determine their effect upon ring oven methods. The factors investigated were turbidity, color, reagent age, reagent temperature, chlorine content and ion level. Standards were prepared by the project chemist and treated with fresh reagent at ambient temperatures at the same time the samples were treated. It was found that reagent age had a significant effect for the ions zinc, magnesium, calcium, and nitrate. Reagent temperature had a significant effect for zinc, magnesium, chloride, fluoride, and nitrate. The results at the high ion concentration were generally less accurate than those at the low ion concentration for copper, zinc, calcium, chloride, sulfate, fluoride, and nitrate.

Qualifications testing was performed for seven of the ten ions: copper, magnesium, calcium, zinc, sulfate, fluoride, and chloride. Lead, iron, and nitrate were deemed insufficiently reliable after fractional factorial testing for further statistical analysis. The high levels of iron present in filters, reagents, etc. caused erratic results. These background levels of iron could not be eliminated. Lead, too, was subject to interference by high background levels of iron, which also reacted with the lead reagent. The nitrate test proved to be too sensitive to the variations in operator technique and experience during the fractional factorial testing to warrant further statistical evaluation.

Three operators analyzed five natural water samples at four ion levels in duplicate for each of the other seven ions. These samples, which were numbered randomly, were compared to the permanent dye transfer standards.

Results of the qualifications tests for six of the ten ions (copper, calcium, zinc, magnesium, chloride, and sulfate) demonstrated that these tests can be used with a high degree of reliability as general screening tools. The results for the fluoride qualifications tests were erratic, apparently because of pH levels of some of the natural waters. For this reason, the ring oven fluoride test does not appear feasible at this time for screening waters.

An investigation of the feasibility of using the ring oven/spot test technique for analysis of water for pesticides and as a tool for rapid general ion scans was also performed. Ring oven reagents with sensitivities on the order of one microgram for the pesticide classes organophosphorus, organochlorines, and arsenicals were found. Successful general scan reagents for cations (pyridylazo-naphthol) and anions (silver nitrate) were tested.

# FOREWORD

This program was undertaken in order to statistically evaluate the ring oven/spot test technique as a method for the field monitoring of water pollutants. The study was performed in fulfillment of Contract No. DAMD17-76-C-6049 and was conducted from April 1, 1976, through September 30, 1977, with Mrs. Jean V. Smith, U. S. Army Medical Research and Development Command, as the Contract Officer. Dr. Eugene Meier served as the Technical Representative of the Contract Officer.

# ACKNOWLEDGEMENTS

The authors are significantly indebted to Dr. Hubert W. Lilliefors for his contribution to the design and analysis of the statistical portion of this research study. Appreciation for assistance throughout various portions of this program is also expressed to Douglas J. Alderson, Kathy G. Benson, John A. DePasquale, Antoine R. Ennis, Marilyn B. Evans, Leslie A. Martin, P. Montoya, and K. Phull.

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## 1.0 INTRODUCTION

The requirement of the United States Army for water test kits centers around the need for accurate, simple, rapid methods for monitoring natural waters in field locations in order to determine their potability. In 1972, the Water Quality Division of the U. S. Army Environmental Hygiene Agency (USAEHA) identified criteria required for such kits. These criteria are summarized in Annex C, Appendix B of the Final Report under USAEHA-EW Study 24-001-71/72. This summary is reproduced as Table 1. The criteria in Table 1 were developed by USAEHA as requirements for the individual components of the Water Quality Analysis Sets being developed by the Army. The simplest set, the Engineer Set, is intended for use by Army engineers in identifying and establishing water supply points. The Preventive Medicine Set is intended for use by preventive medicine personnel in assuring that the water is safe for consumption. The Medical Laboratory Set is intended for use by medical units for more detailed analysis to assure that the water is safe for consumption over longer periods of time.

The ring oven/spot test technique appeared to fulfill the Army's need for such a monitoring method. From May, 1973, to September, 1975, a study was performed (Contract No. DADA17-73-C-3112) by Atlantic Research Corporation in which ring oven procedures were developed and subsequently evaluated using natural water samples. Results of this investigation demonstrated that the ring oven technique is a feasible field approach for the semi-quantitative determination of specific ions in natural water samples. These studies encompassed the entire concentration range, as set forth in the USAEHA-EW Study 24-001-71/72 for each ion investigated during this program.

At the completion of this initial study, it was felt that a more in-depth statistical evalaution was necessary to assess the accuracy, precision and operator variability factor before any final decision as to production of a prototype kit could be made. In addition, it was mutually agreed by the Army and Atlantic Research Corporation that subsequent research emphasis for each ion should revolve around the decision concentrations listed in the USAEHA-EW Study rather than the broader concentration ranges given for each ion. In accordance with these requirements, a statistical evaluation was performed by Atlantic Research from April, 1976, to September, 1977, under Contract No. DAMD17-76-C-6049. The objectives for this program were to:

- Perform fractional factorial and qualifications tests in order to determine the statistical reliability of ring oven tests for ten ions, which were developed under Contract No. DADA17-73-C-3112.
- Determine the feasibility of using the ring oven/spot test technique to determine pesticides in natural waters.
- Determine the feasibility of using the ring oven to perform multiple-ion analysis of natural waters.

## TABLE 1. Summary of Performance Criteria

| Parameter | Range | | | Decision Concentrations | Precision Tolerances | Significance |
|---|---|---|---|---|---|---|
| | ENGR Set | PM Set | MED LAB Set | | | |
| Acidity (mg/l) | 5-500 | 5-500 | 1-500 | 20 | ±5 | In anion column effluent, indicates ion exchange unit column exhaustion. In distillation unit, indicates the presence of sufficient citric acid for tube cleaning. |
| Alkalinity (mg/l) | 5-500 | 5-500 | 5-500 | 120 | ±20 | Indicates the need for more frequent cleaning of distillation equipment. |
| Ammonia (mg/l) | - | 0.01-1.0 | 0.001-0.1 | 0.5 | ±0.1 | Aesthetic maximum which indicates possible contamination of the water. |
| Barium (mg/l) | - | - | 0.1-5.0 | 1.0 | N/A | Medical maximum for long-term consumption. |
| Cadmium (mg/l) | - | - | 0.001-0.1 | 0.01 | N/A | Medical maximum for long-term consumption. |
| Chlorides (mg/l) | 10-1,000 | 10-20,000 | 10-20,000 | 15 | ±5 | Indicate foam carryover, or possible heat exchange leakage in vapor distillation units. |
| | | | | 250 | ±50 | Aesthetic maximum for long-term consumption. |
| | | | | 600 | ±50 | Aesthetic maximum for field consumption. |
| | | | | 1,500 | ±250 | Indicates impracticality of ion exchange; vapor distillation is preferred. |
| Chromium (mg/l) | - | - | 0.01-1.0 | 0.05 | N/A | Medical maximum for long-term consumption. |
| Coagulation | - | - | - | - | - | Allows optimization of chemical feed rates. |
| Color (color units) | 10-200 | 10-200 | 10-200 | 15 | ±5 | Aesthetic maximum for long-term consumption. |
| | | | | 50 | ±10 | Aesthetic maximum for field consumption. Indicates the need for activated carbon. |
| Copper (mg/l) | - | - | 0.1-5.0 | 1.0 | N/A | Medical maximum for long-term consumption. |
| Cyanide (mg/l) | - | - | 0.1-5.0 | 0.2 | N/A | Medical maximum for long-term consumption. |
| | | | | 2.0 | N/A | Medical maximum for field consumption. |
| DO (mg/l) | - | 0.5-15.0 | 0.5-15.0 | 2.0 | ±0.5 | Limit to assist in the control of corrosion problems in steam boilers and water distribution systems. |
| Fluorides (mg/l) | - | 0.1-10.0 | 0.1-10.0 | 0.6 | ±0.2 | Lower operational limit specified for fluoride injection. |
| | | | | 1.5 | ±0.2 | Maximum specified for long-term consumption. |
| | | | | 1.7 | ±0.2 | Upper operational limit specified for fluoride injection. |

TABLE 1. (Continued)

| Parameter | Range ENGR Set | Range PM Set | Range MED LAB Set | Decision Concentrations | Precision Tolerances | Significance |
|---|---|---|---|---|---|---|
| Hardness |  |  |  |  |  |  |
| Total Hardness (mg/l) | 20-9,000 | 20-9,000 | 20-9,000 | 250 | ±50 | Indicates potential scaling in boilers and distillation units. |
| Calcium Hardness (mg/l) | - | - | - | 250 | ±50 | Indicates potential scaling in vapor compression distillation units in conjunction with elevated concentrations of sulfate ion. |
| Magnesium (mg/l) | - | 10-5,000 | 10-5,000 | 125 | ±25 | Aesthetic maximum for long-term consumption. |
|  |  |  |  | 150 | ±25 | Aesthetic maximum for field consumption. |
| Iron (mg/l) | - | 0.1-10.0 | 0.1-10.0 | 0.3 | ±0.1 | Aesthetic maximum for long-term consumption. |
| Lead (mg/l) | - | 0.05-1.0 | 0.01-1.0 | 0.05 | ±0.005 | Medical maximum for long-term and field consumption. |
| Mercury (mg/l) | - | - | 0.001-0.1 | 0.002 | N/A | Medical maximum for long-term consumption. |
| Nitrates (mg/l) | - | 1.0-20.0 | 1.0-20.0 | 10 | ±2 | Medical maximum for long-term and field consumption. |
| pH (pH units) | 3.0-11.0 | 3.0-11.0 | 1.0-14.0 | 5.5 | ±0.2 | Maximum density of ferric hydroxide floc which indicates maximum settling rate. |
|  |  |  |  | 5.8 | ±0.2 | Aesthetic minimum for long-term consumption. |
|  |  |  |  | 8.1 | ±0.2 | Minimum acceptable for the oxidation of ferrous iron. |
|  |  |  |  | 9.2 | ±0.2 | Aesthetic maximum for long-term consumption. |
| Selenium (mg/l) | - | - | 0.001-0.1 | 0.01 | N/A | Medical maximum for long-term consumption. |
| Sulfates (mg/l) | 100-3,000 | 100-3,000 | 10-3,000 | 250 | ±50 | Aesthetic maximum for long-term consumption. |
|  |  |  |  | 400 | ±100 | Aesthetic maximum for field consumption. |
|  |  |  |  | 2,700 | ±300 | As sulfates approach 3,000, water with high calcium concentrations could produce scale in standard vapor compression distillation units. |

TABLE 1. (Continued)

| Parameter | Range<br>ENGR Set | Range<br>PM Set | Range<br>MED LAB Set | Decision Concentrations | Precision Tolerances | Significance |
|---|---|---|---|---|---|---|
| TDS (mg/l) | 1-5,000 | 1-35,000 | 1-35,000 | 50 | ±10 | An ion exchange effluent in the 30-80 range indicates exhaustion of the resin. |
| | | | | 500 | ±50 | Aesthetic maximum for long-term consumption. |
| | | | | 1,500 | ±100 | Aesthetic maximum for field consumption. |
| Turbidity (JTU) | 0.1-5.0 | 0.1-5.0 | 0.1-500 | 0.1-0.5 | ±0.1 | An increase in turbidity will focus attention on faulty coagulation or filtration. |
| | | | | 5.0 | ±1.0 | Aesthetic maximum for long-term and field consumption. |
| | 25-500 | 10-500 | | 500 | ±100 | Use of a pre-settling step is indicated in field water treatment. |
| Zinc (mg/l) | - | 1-20 | 1-20 | 5 | ±1.0 | Aesthetic maximum for long-term consumption. |

## 2.0 BACKGROUND

During the period from May 1, 1973, to September 30, 1975, Atlantic Research performed a study to determine the feasibility of using the ring oven/spot test technique for monitoring specific cations and anions in natural waters (1). It was anticipated that these monitoring techniques, if acceptable, would eventually be used to determine *in situ* the potability of various natural waters.

Since the ring oven/spot test technique was envisioned as being used by relatively untrained personnel, it was felt that the final kit should utilize the simplest, most direct, and foolproof hardware items possible. This would include not only the ring oven, but also sample reagent delivery systems and filter papers. Compactness and ruggedness were also of concern since the kit might have to be carried by combat troops in the field. In order to determine the absolute feasibility of the ring oven technique for use by the Army, a concurrent program of chemical and methods screening was made. It was felt that the entire study should be geared toward the "average person" and not exclusively toward the chemical aspects. It would accomplish little to have adequate chemistry, coupled with cumbersome, difficult hardware. The results of this work, which was performed under Contract No. DADA17-73-C-3112, are summarized in the following paragraphs. (This work is described in detail in Reference 1.)

The eight ions considered during the first year of contract effort were magnesium, zinc, iron, lead, nitrate, sulfate, fluoride and chloride. The Army felt that these ions offered the greatest potential for development of successful ring oven procedures. During the second year's effort, the ions copper, calcium, cadmium, chromium, manganese, cyanide and phosphate were added to the first group.

The concentration range of interest for each of these ions was selected to fulfill the requirements of the Preventive Medicine (PM) kit, as shown in Table 1. Standards were selected to encompass the entire range of concentrations as stated in the specifications of the PM kit (Table 1). The colorimetric detection reagents chosen were able to show a colorimetric intensity gradation over the entire concentration range of interest for each ion investigated. In fact, colorimetric detection reagents were selected based upon their ability to discriminate over the entire concentration range of interest, rather than to determine small concentration changes. Preliminary feasibility tests on natural water samples demonstrated that the procedures and ring oven techniques developed during this study were worthy of further investigation for the ions zinc, copper, calcium, iron, lead, magnesium, nitrate, fluoride, chloride, and sulfate. Suitable reagents of sufficient sensitivity were not located for the other ions. A brief review of the ring oven procedure and results of the initial study are given in Appendix A of this report.

## 3.0 EXPERIMENTAL APPROACH

### 3.1 Selection of Permanent Standard Values

At the initial meeting under this contract, it was agreed upon by both the Army and Atlantic Research that the purpose of the program would be better served by evaluating ring oven performance in the critical areas around the decision concentrations rather than over the entire concentration ranges set forth in the USAEHA-EW study. This conclusion was based upon the fact that the values around the decision concentrations would be the most useful criteria in establishing water potability. In most cases, the decision value selected as being most important was that value given as the maximum for long-term consumption, except for chloride, magnesium and sulfate, where the field consumption value was considered suitable. The most desirable values for the standard rings were considered to be the decision level, plus or minus the tolerance values for the PM kit. (See Table 1, pp. 3 - 5.) These tolerance values were designed to indicate the maximum permissible concentration of a particular ion in water. At concentration values above the decision concentration plus the tolerance value, the water should not be used for drinking purposes because of health hazards or aesthetic reasons.

In order to establish tolerance values that would produce rings of sufficient intensity difference for each of the ions investigated, various standards were prepared which bracketed the decision concentration of each ion. The standards were then subjected to the ring oven procedure and the concentration increments adjusted around the decision level until the minimum tolerance values capable of establishing a distinct color gradation were established. This effort, which is described more fully in Section 5.0, frequently consisted of procedural adjustments, so that rings of sharper intensity and better intensity differences were produced. The initial standard values are shown in Table 2.

During the period when this preliminary standard selection was carried out, methods of preparing permanent standards were also being investigated. In the course of this effort, which is further described in Section 3.2, it was found that subtle ring gradation differences were present

### TABLE 2. Initially Proposed Standard Concentrations (Decision Concentrations Underlined)

| Ion | ppm | | | |
|---|---|---|---|---|
| Magnesium* | 75 | 125 | 175 | 225 |
| Zinc | 3 | 5 | 7 | 9 |
| Iron | 0.1 | 0.3 | 0.5 | 0.7 |
| Copper | 0.5 | 1.0 | 1.5 | 2.0 |
| Calcium | 150 | 250 | 350 | 450 |
| Lead | 0.01 | 0.05 | 1.00 | 5.0 |
| Nitrate | 7 | 10 | 13 | 16 |
| Fluoride | 0.6 | 1.0 | 1.5 | 5.0 |
| Chloride | 250 | 400 | 600 | 800 |
| Sulfate | 200 | 300 | 400 | 500 |

*Initially the magnesium decision level was to be the long-term consumption level; this was dropped in favor of the field consumption level later in the program.

which could not be easily reproduced by common methods (for example, by an artist). This led to serious questions about the reproducibility of the ring oven gradations in the context of the tolerance values previously established by simply obtaining a color gradation between the decision concentration and the minimum possible concentration intervals on either side of the decision limit.

Consequently, several tests were performed to establish the reproducibility of the ring oven technique within the initial tolerance limits that had been established as being those values which first produced a distinguishable color gradation between rings. (See Table 2, p. 9.) The evidence was conclusive: operator variability was a significant factor, and the ring oven standards could not be matched to duplicate standards prepared at the same time. The color gradation between rings prepared at the concentrations shown in Table 2 was evident in each set of standards examined. If, however, one set of standards was used to determine concentrations of individual members of a second set of unlabeled identical standards, the values for the second set could not be determined accurately. Some deviation resulted from subtle changes in ring width. Thus, color-intensity/ring width variances were magnified when concentration gradients were small, as in working with close tolerances around the decision concentration.

Therefore, to avoid introducing errors due to operator variance, it was decided to increase standardization increments between standards until the variance fell within well defined limits. It was apparent, however, that the primary cause of ring width effects is unavoidable variance in operator technique from one ring to the next. While the variance of a single operator's technique was incorporated into the selection of standards shown in Table 2, it was imperative that the variability in techniques of differing operators be considered before permanent standards were prepared. Operator variability tests were performed to accomplish this.

During these tests, two operators performed approximately 20 synthetic water sample tests for each ion in which the sample concentration was unknown to the operator. At the same time, samples were prepared and treated with reagent by the Project Chemist for comparison. If the results of the comparison were not satisfactory, the standard increments were broadened, and the two-operator analyses repeated. Standard values obtained during this effort were then submitted to the Army for their approval. These standards are shown in Table 3.

At this time, the Army and Atlantic Research Corporation agreed that some additional refinement should be performed on the same standards which had been previously submitted to limited operator variability testing. Such refinement would ideally bring the bracketing values closer around the decision level. Limited work was performed in the laboratory in order to check the refined values.

At the same time, some questions arose as to whether better results could be obtained when the decision level was not included as part of the standard ring set. This might allow a tighter bracketing of the decision level with the same minimum ring differentiation. For example, if a minimum visible gradation increment of 2 ppm could be seen, eliminating the decision level could allow the use of two standards, 1 ppm on each side of the absent decision level, while still maintaining the 2 ppm gradation increment. It was decided to perform limited laboratory tests to prove or disprove this theory before a final decision concerning standard values was made.

In order to facilitate this decision, tests were performed using the zinc and copper ions and two sets of standard rings: one set including the decision level, and the other set without this value, but including rings more closely bracketing it. The results of these tests are given in Tables 4 and 5. As can be seen from the tables, no apparent advantage was obtained when the decision level was excluded from both ions. In fact, readings with the decision level were always as good as (or better than) those obtained when this value was eliminated. Thus, it was decided to leave the decision level in the standard sets.

The standard values obtained after the limited refinement testing had been accomplished were submitted to the Army. These standards, which are shown in Table 6, were subsequently approved and were used for the preparation of permanent standards.

TABLE 3. Suggested Standard Levels After Limited Operator Variability Testing (Decision concentrations are underlined.)

| Ion | ppm | | | |
|---|---|---|---|---|
| Zinc | 1 | 5 | 9 | 15 |
| Copper | 0.1 | 1 | 4 | 8 |
| Calcium | 50 | 250 | 450 | |
| Magnesium | 25 | 125 | 500 | 1000 |
| Chloride | 15 | 250 | 600 | 1250 |
| Sulfate | 50 | 250 | 1000 | 3000 |
| Nitrate | 5 | 10 | 20 | 30 |
| Iron | *Blank | 0.3 | 0.7 | 2.0 |
| Fluoride | *Blank | 0.5 | 1.5 | 5.0 |
| Lead | 0.01 | 0.05 | 1.0 | |

*Blanks consisted of deionized water plus all reagents. Some background color was produced in the ring.

TABLE 4. Effect of Presence of Decision Level in Standard Set - Copper

**COPPER**

| Sample | Actual Concentration | Without Decision Concentration Ring Oven Results Operator #5 | Without Decision Concentration Ring Oven Results Operator #6 | With Decision Concentration Ring Oven Results Operator #5 | With Decision Concentration Ring Oven Results Operator #6 |
|---|---|---|---|---|---|
| R | 2.0 | 1.5 | 0.5 | 1.5 | 1.0 |
| U | 1.5 | 1.3 | 1.0 | 1.0 | 1.0 |
| T | 0.9 | 1.5 (0.5)* | 0.2 (1.0) | 0.9 (0.5) | 0.5 (1.0) |
| S | 1.1 | 0.5 (0.5) | 0.2 (3.0) | 1.0 (0.5) | <0.5 (3.0) |
| K | 4.0 | 4.0 | 2.0 | 3.0 | 3.0 |
| A | 1.4 | 1.5 | 0.5 (2.0) | 1.5 | 0.5 (2.0) |
| D | 0.1 | 0.1 | 0.1 | <0.5 | <0.5 |
| P | 0 | 0 | 1.0 (<0.1) | <0.5 | 1.0 (<0.5) |
| F | 5.0 | >4.0 | >4.0 | 4.0 | >4.0 |
| CC | 1.3 | 1.0 | 0.5 | 1.0 | 0.5 |
| DD | 0.7 | 0.5 | 0.5 | 0.5 | 0.5 |
| BB | 1.8 | 1.5 | 1.5 | 1.5 | 2.0 |
| AA | 0.9 | 0.5 | 1.0 | 0.9 | 1.0 |
| FF | 1.0 | 1.4 | 0.5 | 1.0 | 0.5 |
| EE | 0 | <0.1 | - | <0.5 | - |

| | Without Decision | With Decision |
|---|---|---|
| Standards | 0.1 - 0.5 - 1.5 - 4.0 | 0.5 - 1.0 - 2.0 - 4.0 |

*Parentheses represent repeat analysis

TABLE 5. Effect of Presence of Decision Level in Standard Set - Zinc

ZINC

| Sample | Actual Concentration | Without Decision Concentration Ring Oven Results Operator #5 | Without Decision Concentration Ring Oven Results Operator #6 | With Decision Concentration Ring Oven Results Operator #5 | With Decision Concentration Ring Oven Results Operator #6 |
|---|---|---|---|---|---|
| A | 0 | <1 | <1 | 1 | <1 |
| B | 6 | 7 | 3 | 4 | 6 |
| C | 3 | 3 | <1 (3)* | 5 | <1 (3) |
| D | 5 | 8 (11) | 2.5 (11) | 9 (12) | 2.5 (11) |
| E | 1 | 1 | 1 | 2 | 1 |
| F | 10 | 11 (>11) | 10 | 14 (15) | 9 |
| G | 4 | 4 | 2.5 | 4 | 5 |
| H | 2 | 1 (1) | <1 (1) | 1 (1) | <1 (1) |
| I | 8 | 11 (11) | 7 | 9 (15) | 6 |
| J | 11 | >11 ( 11) | 3 (>11) | 15 | 5 .(15) |
| K | 9 | 11 | 11 | 15 | 9 |
|  |  | **Standards** |  | **Standards** |  |
|  |  | 1 - 3 - 7 - 11 |  | 1 - 5 - 9 - 14 |  |

*Parentheses represent repeat analysis.

TABLE 6. Permanent Standard Levels (ppm)
(Decision concentrations underlined)

| Ion | ppm | | | |
|---|---|---|---|---|
| Zinc | 2 | 5 | 8 | 11 |
| Copper | 0.5 | 1 | 2 | 4 |
| Calcium | 50 | 250 | 450 | |
| Magnesium | 50 | 150 | 300 | 600 |
| Chloride | 200 | 400 | 600 | 1000 |
| Sulfate | 50 | 400 | 1000 | 2700 |
| Nitrate | 6 | 10 | 14 | 25 |
| Iron | *Blank | 0.3 | 0.7 | 2 |
| Fluoride | *Blank | 0.5 | 1.5 | 5 |
| Lead | 0.01 | 0.05 | 1.0 | |

*Blanks consisted of deionized water plus all reagents. Some background color was produced in the ring.

## 3.2 Preparation of Permanent Standards

During the initial contract meeting, it was also decided that permanent standards should be prepared for use in the qualifications testing in order to determine accuracy, precision and operator variability. Permanent standards which were easily mass-produced and were stable over a long period of time were necessary, should the technique prove suitable for kit production. Several methods for production of the standards were investigated in order to insure that these conditions were met in the optimum manner. The following paragraphs describe this investigation.

### 3.2.1 Color Photography

Color photography was used during the initial study in order to generate exemplars for reporting purposes. At that time, difficulty was encountered in reproduction of the color prints due to changes in various lots of film development chemicals. This made reproducibility by color photography suspect. In addition, color prints are not stable with respect to time. For these reasons, color photography was eliminated from consideration.

### 3.2.2 Colored Ink Reproduction

Consideration was given to using colored inks to reproduce the ring gradations, either by a representation of the total filter paper or by the use of colored blocks matching the rings in both hue and intensity.

The La Motte Company of Chestertown, Maryland, which is heavily involved in the manufacture of standards for water test kits, test papers, etc., was contacted with respect to production of colored ink standards for the ring oven. The photographs of the rings from the first year's final report were sent for examination. The initial response from La Motte concerning the preparation of permanent color standards was negative. They reported that the photographs of the rings which we sent to them differed from their expectations, and that they had no method for reproducing such colors.

We then consulted with the Atlantic Research Corporation Art Department. Some promise was exhibited by a technique using varying intensities of water color paints sprayed on a flat surface paper that matched individual ring background colors. It was found, however, that subtle ring gradations existed, which could not be reproduced successfully by the artists. For example, calcium rings varied in intensity not by changing color, but by changing width. Some success was obtained with circles (14 mm in diameter) with circumferences of varying widths, but of a single color, drawn with a compass. The same procedure would probably be required for sulfates and chlorides. In the case of magnesium, however, ring gradations over the decision concentration neighborhood were not due to a change in ring width or in color, but to minute changes in ring intensity which were extremely difficult to duplicate with inks or paints.

### 3.2.3 Dye Transfer Process

A method which appeared to show great promise involved the use of a color separation of color transparencies and a four-color press, or a dye transfer process. The stability of the color separations, which are prepared on black-and-white film using three colored filters, appeared to offer a definite advantage since the resulting silver density images have an estimated stable life of hundreds of years, when properly processed and stored.

Upon the recommendation of Mr. Don Fisk, a photographic specialist with the U. S. Government, a decision was made to use dye transfer as the method for preparation of the permanent standards. Multiple sets of the rings were prepared and photographed as 4-inch by 5-inch transparencies. For convenience, transparencies were prepared in two groups, thus allowing qualifications testing of the first set to be performed while permanent standards for the second set were in preparation.

Berkey K and L, Inc., of New York, which is one of only two firms on the East Coast performing dye transfer work, prepared the dye transfer prints. The overall quality of the final prints was excellent, and as discussed in the preceding paragraphs, the stability of the images used in preparing the dye transfers is superior to the stabilities involved in other method. Each proof dye transfer was obtained at a cost of $145, with a $20 charge for each additional dye transfer print. The dye transfer prints of the standard rings were used in the qualifications tests to determine accuracy, precision, and operator variability, as discussed in Section 5.0.

### 3.3 Selection of Ion Concentrations for Fractional Factorial and Qualifications Testing

As with the selection of permanent standard concentration levels, it was desirable that the selection of concentrations for the waters used in statistical testing closely reflect areas bracketing the various decision concentrations. The Army and Atlantic Research, using the permanent standards as guidelines, mutually selected the values shown in Table 7 as being suitable for qualifications analysis. As can be seen from the table, four ion concentrations for each ion were necessary for the qualifications testing. These four ion concentrations were selected to bracket the decision concentration as closely as the ring oven method would allow. Two ion test concentrations were placed below the decision level, and two above. The highest concentration value for each ion was considered to be of particular importance. These high values were chosen so that they were in excess of acceptable water potability standards.

On the other hand, the fractional factorial testing required two ion concentrations for each ion. With the Army's approval, it was decided that the highest and lowest values of each ion's qualifications test concentrations be used as the fractional factorial test levels. These values are given in Table 8.

### 3.4 Investigation of Packaging Methods for Reagents

It was initially planned to perform fractional factorial and qualifications testing using reagents packaged in a manner suitable for use in an actual field test kit. The use of sealed, metered aerosol sprays appeared to be the most efficient method for reagent application in several

TABLE 7. Suggested Test Water Concentrations (ppm) - Qualifications Testing

| | | | | |
|---|---|---|---|---|
| **Zinc** | 1 | 3 | 7 | 10 |
| **Copper** | 0.4 | 0.7 | 1.5 | 3.0 |
| **Calcium** | 50 | 175 | 350 | 600 |
| **Magnesium** | 40 | 100 | 200 | 400 |
| **Chloride** | 300 | 500 | 800 | 1100 |
| **Sulfate** | 40 | 200 | 600 | 1200 |
| **Nitrate** | 4 | 8 | 12 | 16 |
| **Iron** | Blank | 0.2 | 0.5 | 1.0 |
| **Fluoride** | 0.4 | 0.6 | 1.7 | 6.0 |
| **Lead** | 0.02 | 0.07 | 0.4 | 1.1 |

TABLE 8. Suggested Test Water Concentrations (ppm) - Fractional Factorial Testing

| | | |
|---|---|---|
| Zinc | 1 | 10 |
| Calcium | 50 | 600 |
| Magnesium | 40 | 400 |
| Copper | 0.4 | 3 |
| Iron | Blank | 1 |
| Lead | 0.02 | 1.1 |
| Sulfate | 40 | 1200 |
| Chloride | 300 | 1100 |
| Nitrate | 4 | 16 |
| Fluoride | 0.4 | 6 |

cases. This would allow the delivery of known amounts of reagent, thus preventing over application of colorimetric indicators and the resultant masking of ring colors.

Several specialists in the field of aerosol packaging were consulted with respect to metered sprays. It was found that the use of a freon propellant with a water-based solution might lead to difficulties. The low solubility of freon in water could cause the freon to sink to the bottom, where it would cease to function as a propellant. While this could be compensated for by using emulsifying agents, determination of the proper emulsifier is often time consuming. To circumvent this, attempts were made to change solvents from 100 percent water to organics or mixed water-organics. However, it was felt that it was better not to introduce additional variables into the analysis scheme at the last moment, such as a change in reagent composition. For this reason, any sprayed reagent was applied by using aerosol jet packs, as in the past.

# 4.0 METHODS AND MATERIALS

## 4.1 Apparatus

The apparatus used during this program is briefly described in the following sections. A more complete discussion of the various types of equipment which were evaluated for ring oven use is given in Reference 1.

### 4.1.1 Ring Oven

The ring ovens used during this program were Thomas Air Pollution Trace Ovens, Model E-10. Each ring oven was Teflon coated by Atlantic Research Corporation on the surfaces that come into contact with the filter papers. This was done in order to prevent corrosion of the original ring oven surface which might result in contamination of samples during analysis.

### 4.1.2 Pipets

The pipets utilized were Pipetman micropipets, P-20, obtained from Rainin Instrument Company. These pipets are digital with disposable polyethylene tips to prevent contamination.

### 4.1.3 Filters

During the previous contract effort, Whatman #40 filter papers were used exclusively for ring oven work. At the conclusion of that effort, however, it was discovered that the newer lots of Whatman #40 filter papers were contaminated with iron and chloride species. Therefore, further investigation was performed during this study to determine the optimum filter type for ring oven use.

Various kinds of synthetic fiber filters were considered, such as Millipore's Duralon nylon filters. These appeared to be unsuitable for several reasons. The thermal stability of the nylon filters was suspect, as they are not recommended for use above 75°C. Ring oven procedures for water based samples and reagents require a temperature of approximately 100°C for efficient evaporation and ring formation. In addition, synthetic fiber filters, in general, do not have the required capillarity for ring oven use. These factors would seem to eliminate synthetic fiber filters from consideration.

Whatman #541 filter papers were also tested. These papers were reported by the manufacturer to contain one-fifth as much iron as the #40 grade. Testing of the #541 paper showed considerably less iron and chloride than the #40 papers contained. Iron content, especially, was markedly reduced. Some residual iron was present, which appears to be inevitable regardless of the type of filter papers used. The Whatman #541 papers, however, exhibited capillary action inferior to that shown by the Whatman #40 papers, which meant that ring formation on the #541 type was inferior. For this reason, it was decided to use Whatman #40 papers for all ring oven testing except chloride and iron, for which Whatman #541 papers were used.

## 4.2 Preparation of Standard Solutions

All standard solutions for cations and anions were prepared by diluting appropriate known volumes of primary standard solutions in volumetric flasks with deionized water. The primary standards were either 1000 ppm solutions purchased from chemical companies, or were prepared by weighing known amounts of dried salts and dissolving these in deionized water.

Pesticide standards were prepared in the same manner, except that organic solvents were used instead of water in order to obtain standards solutions of sufficient concentrations. This was necessary due to the relatively low solubilities of organochlorines in water.

## 4.3 Fractional Factorial Testing

The fractional factorial tests were intended to determine the effect of varying the factors (experimental conditions) listed in Table 9. Two levels for each factor were selected. These levels, which were chosen in consultation with the Army, were, for the most part, the extremes given for the parameters listed in Table 1 (page 3). Levels for factors (4) and (5) were chosen by the Army as being of particular interest for their purposes. Two levels of ion concentration, as shown in Table 9, were also utilized. The level of ion concentration was considered as a sixth factor.

TABLE 9. Levels of Variables, Fractional Factorial Testing

| Variable | Low Level | High Level |
|---|---|---|
| 1) Turbidity (JTU) | 0.1 | 5 |
| 2) Color (Standard Units) | 10 | 100 |
| 3) Reagent Temperature (°C) | 10 | 40 |
| 4) Reagent Age | 1 Hour | 6 Months |
| 5) Chlorine Concentration (mg/l) | 0 | 10 |
| 6) Ion Concentration (ppm) | | |
| Zinc | 1 | 10 |
| Calcium | 50 | 600 |
| Magnesium | 40 | 400 |
| Copper | 0.4 | 3 |
| Iron | 0 | 1 |
| Lead | 0.02 | 1.1 |
| Sulfate | 40 | 1200 |
| Chloride | 300 | 1100 |
| Nitrate | 4 | 16 |
| Fluoride | 0.4 | 6 |

A one-half replicate (32 of the possible combinations of experimental conditions) was used, making two measurements for each of the combinations of experimental conditions measured by a single operator. This allowed for an unbiased estimate of the experimental error, based upon the repeated measurements, but still allowed for testing for the significance of the six main effects and the fifteen first order interactions between the factors. It also allowed for a test to determine whether certain higher order interactions were significant.

The measurements were made according to Plan 6A.6 by Cochran and Cox.(2) Using the notation in Cochran and Cox, the measurements listed in Table 10 were made. In order to determine which of the two levels for each of the six factors (1, 2, 3, 4, 5, 6) was to be used, one looks at the symbolic representative in the Table. If the number for that factor was present, the second level for that factor was used. If the number for that factor was absent, the first level for that factor was used. Thus, for the measurements 1,3,5,6 in the table, the second levels for the factors 1,3,5,6 were used and the first level for the factors 2,4.

An adjustment in the test matrix was required, however, due to the interaction between factor 2, sample color, and the high level of factor 5, chlorine concentration. It was found that the chlorine effectively decolorized the water. This, of course, meant that neither the color nor the chlorine in the samples was at the level of interest, as both quantities decreased due to chemical reactions. It was decided to eliminate color from those samples containing chlorine. This permitted the analysis of samples with a chlorine level, which was of greater interest to the Army. (The adjustment was considered in the analysis of the fractional factorial test results.) The elimination of color from chlorinated samples is reflected in Table 11, which gives a point-by-point interpretation of the test design.

### 4.3.1 Preparation of Samples and Reagents for Fractional Factorial Testing

The actual values of each parameter examined in the fractional factorial testing are given in Table 9, along with each ion concentration

TABLE 10. Experimental Design for Fractional Factorial Testing(2)

| | | | |
|---|---|---|---|
| * | 1,2,5,6 | 1,3,4,5 | 2,3,4,6 |
| 1,2 | 5,6 | 1,3,4,6 | 2,3,4,5 |
| 1,3 | 4,5 | 1,2,4,6 | 2,3,5,6 |
| 2,3 | 4,6 | 1,3,5,6 | 1,2,4,5 |
| 1,5 | 2,6 | 3,4 | 1,2,3,4,5,6 |
| 1,6 | 2,5 | 1,2,3,4 | 3,4,5,6 |
| 1,4 | 3,5 | 1,2,3,5 | 2,4,5,6 |
| 2,4 | 3,6 | 1,2,3,5 | 1,4,5,6 |

* = all factors at lower levels
1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

TABLE 11. Sample Composition for Fractional Factorial Tests

| Sample No. | Table Rep. | Turbidity | Color | Reagent Temp. (Degrees) | Reagent Age | Chlorine Conc. | Ion Conc. |
|---|---|---|---|---|---|---|---|
| a | (1,2,3,4,5,6)* | 0.1 | 10 | 10 | 1 hr | 0 | l |
| b | 1,2 | 5.0 | 100 | 10 | 1 hr | 0 | l |
| c | 1,3 | 5.0 | 10 | 40 | 1 hr | 0 | l |
| d | 2,3 | 0.1 | 100 | 40 | 1 hr | 0 | l |
| e | 1,5 | 5.0 | 0 | 10 | 1 hr | 10 | l |
| f | 1,6 | 5.0 | 10 | 10 | 1 hr | 0 | h |
| g | 1,4 | 5.0 | 10 | 10 | 6 months | 0 | l |
| h | 2,4 | 0.1 | 100 | 10 | 6 months | 0 | l |
| i | 1,2,5,6 | 5.0 | 0 | 10 | 1 hr | 10 | h |
| j | 5,6 | 0.1 | 0 | 10 | 1 hr | 10 | h |
| k | 4,5 | 0.1 | 0 | 10 | 6 months | 10 | l |
| l | 4.6 | 0.1 | 10 | 10 | 6 months | 0 | h |
| m | 2,6 | 0.1 | 100 | 10 | 1 hr | 0 | h |
| n | 2,5 | 0.1 | 0 | 10 | 1 hr | 10 | l |
| o | 3,5 | 0.1 | 0 | 40 | 1 hr | 10 | l |
| p | 3,6 | 0.1 | 10 | 40 | 1 hr | 0 | h |
| q | 1,3,4,5 | 5.0 | 0 | 40 | 6 months | 10 | l |
| r | 1,3,4,6 | 5.0 | 10 | 40 | 6 months | 0 | h |
| s | 1,2,4,6 | 5.0 | 100 | 10 | 6 months | 0 | h |
| 5 | 1,3,5,6 | 5 | 0 | 40 | 1 hr | 10 | h |
| u | 3,4 | 0.1 | 10 | 40 | 6 months | 0 | l |
| v | 1,2,3,4 | 5.0 | 100 | 40 | 6 months | 0 | l |
| w | 1,2,3,6 | 5.0 | 100 | 40 | 1 hr | 0 | h |
| x | 1,2,3,5 | 5.0 | 0 | 40 | 1 hr | 10 | l |
| y | 2,3,4,6 | 0.1 | 100 | 40 | 6 months | 0 | h |
| z | 2,3,4,5 | 0.1 | 0 | 40 | 6 months | 10 | l |
| aa | 2,3,5,6 | 0.1 | 0 | 40 | 1 hr | 10 | h |
| bb | 1,2,4,5 | 5.0 | 0 | 10 | 6 months | 10 | l |
| cc | 1,2,3,4,5,6 | 5.0 | 0 | 40 | 6 months | 10 | h |
| dd | 3,4,5,6 | 0.1 | 0 | 40 | 6 months | 10 | h |
| ee | 2,4,5,6 | 0.1 | 0 | 10 | 6 months | 10 | h |
| ff | 1,4,5,6 | 5.0 | 0 | 10 | 6 months | 10 | h |

*Refer to Table 10, p. 25, for an explanation of symbols used.

investigated. The following discussion describes how each of the desired characteristics was achieved in the individual samples investigated during the fractional factorial testing.

Turbidity was simulated through the use of a kaolin suspension. The turbidity of this suspension was read using a Jackson Candle Turbidimeter. Appropriate aliquots of this suspension were then used to give the two turbidity levels of interest.

It was important that the species used to produce color be water soluble rather than a suspended material, as it was required that the color migrate to the ring. Therefore, food coloring was used to prepare the colored water. A standard colored water solution ($KPtCl_6$ and $CoCl_2$) was matched spectrophotometrically with the food coloring solution in order to insure the latter's accuracy. (Food coloring was used because of the potential interferences from the metals in ring oven procedures and the chloride in the cobalt-platinum solution.)

Five milliliters of a solution of household bleach was diluted to one liter with deionized water, and standardized using iodometric mehtod I from Standard Methods for the Examination of Water and Wastewater,$^{(3)}$ for residual chlorine. This standardization was repeated at regular intervals due to the possibility of the chlorine levels changing in the solutions. Samples containing chlorine were stored in brown glass bottles, and analyzed on the same day that they were prepared.

Ion concentrations were obtained by adding appropriate known amounts of standard ion solutions to the known amounts of turbidity, color, and chlorine solutions, then diluting to a known volume in a volumetric flask with deionized water. Samples were not analyzed by standard methods after spiking with known amounts of ions.

Reagents were aged for ten months at 90°F and 90% relative humidity in a Blue M CFR-7552 Temperature/Humidity Cabinet. The longer aging period (ten months, as opposed to six months as originally planned) was due to scheduling changes which were found to be necessary during contract effort. Solid reagents were stored in sealed polyethylene-lined packets. Liquid reagents were stored in amber bottles.

### 4.3.2 Treatment of Fractional Factorial Procedures

The following paragraphs present a general description of the statistical analysis of the fractional factorial tests performed during this program. The actual results and their interpretation for each ion of interest are presented in Section 5.0.

For each ion, 32 water samples were prepared. An operator made two measurements on each water sample. The order in which the 64 measurements were made was randomized. The set of all measurements was in the form of a half replicate of a $2^6$ factorial. Since the results for the high ion concentrations seemed quite different from those for the low ion concentrations, separate analyses were made for the sets of measurements at the two ion levels, as well as for an overall analysis at all ion levels.

Since this is a one-half replicate of a full factorial, there will be an "alias" for each factor and interaction listed in the tables. The "alias" can be found for each factor and interaction as the interaction of all the other factors. Thus, for the factor 2, the "alias" is the fourth order interaction involving factors 1, 3, 4, 5, 6; for the interaction 1,3, the "alias" is the third order interaction of the factors 2, 4, 5, 6. The term "alias" is used since either the factor or the interaction listed in the table or its "alias" are tested. Thus, if factor 2 had a significant effect, it is possible (though highly unlikely) that, in fact, it is its alias which has a significant effect. In general, the higher order interactions can be assumed to be (and are) negligible. When tests are performed at just one ion concentration, the "aliases" are found in the same way, and are, in fact, the same except that factor 6, the ion level, is no longer involved. Thus, the "alias" for factor 2 becomes the third order interaction involving factors 1, 3, 4, 5.

In all cases, the actual ion concentration was subtracted from the value measured using the ring oven. Thus, the analysis was performed on the error in measurement. Due to the orthogonality of the design, this has no effect on the statistical tests, except for factor 6, ion concentration. For all other factors and interactions, the results would be the same if the original measurements were used.

One problem in the analysis was the question of the residual mean-square (the divisor for the F ratio). If a new water sample had been utilized for the second measurements on each water sample, then

$$S_p^2 = \frac{\sum_{i=1}^{32} (X_{1i} - X_{2i})^2}{64}$$

would have been the residual mean square. (In the analysis, the average of the two measurements was used at each combination of the various factor levels, so $S_p^2/2$ would have been the appropriate residual mean square.

Even though the same water samples were used (and, therefore, it was not truly a replication of the experiment), the quantity $S_p^2/2$ was used for the residual mean square, which would tend to inflate F ratios. Analyses were also performed, however, using the "lumped" higher order interactions (which provided 10 degrees of freedom). If, in fact, there were no higher order interactions, this would be valid. If there were higher order interactions this would tend to over-estimate the true residual mean square, and, therefore, to deflate the F ratios. As can be seen from the tables in Section 5.0, the conclusions one draws are about the same either way. For the data separated according to ion level, it was necessary to use the $S_p^2/2$ for residual mean square, because of the small number of samples examined.

## Tables Presented in Section 5.0 Describing Fractional Factorial Tests Analyses

For each ion subjected to fractional factorial testing, several tables are given in Section 5.0. A description of these tables is presented in the folowing paragraphs.

### a) Analysis of Variance Tables Using All Observations

These tables list the various factors by numbers, together with that part of the sum of squares which is attributable to that factor. Table 9 (p. 23) lists the factors corresponding to the numbers in the Analysis of Variance tables. When two numbers are given together for a factor that indicates the interaction of the corresponding factors, e.g., 2, 4; 2 represents the interaction of color and 4 represents the reagent age.

The F value is calculated by dividing the sum of squares (which is also the mean square since there is only one degree of freedom for each factor) by $S_p^2/2$ which is used for the residual mean square. A large value for F indicates that the corresponding factor has a significant effect. In order to determine whether a factor has a significant effect, the calculated F value is compared to a table of critical values for the F distribution (using one degree of freedom for the numerator and 32 degrees of freedom for the denominator). If it exceeds the critical value for a given significance level, then the factor is judged significant at that level. Following the F value, a single asterisk (*) signifies that it was significant at the 0.05 level, but not at the 0.01 level; two asterisks (**) signifies that it was significant at the 0.01 level, in which case it is termed highly significant.

"Significant at the 0.05 level" means that if the factor actually had no effect, there would be only one chance in twenty (a probabilty of 0.05) of obtaining such a large F value. Similarly, "significant at the 0.01 level" means that if the factor actually had no effect, there would be only one chance in a hundred (a probability of 0.01) of obtaining such a large F value. For instance, for the iron ion (Table 63a, p. 134), the F value for factor 6 has two asterisks. From Table 9 (p.23), we see that factor 6 corresponds to the different ion concentrations. We conclude that there is a highly significant difference in the measurement accuracy at the two ion concentrations.

b) <u>Tables of Average Errors for Factor Levels</u>

Tables are also given in Section 5.0 for the average errors for the high and low levels of each factor. Using all observations for factor 1 (Table 63c, p. 136) for instance, we see that the average error of all measurements made with factor 1 at its high level is -0.256. From Table 9 (p. 23), factor 1 is turbidity and the high level of turbidity is 5 JTU.

Thus, for all 32 measurements (16 water samples) with turbidity at its high level, the average error (measured in ion level minus actual ion level) was 0.256.

### c) Analysis of Variance Tables for Individual Ion Concentrations

Analysis of Variance Tables are also given separately for those measurements made at the high ion concentrations and those made at the low ion concentrations. The only difference here is that only 16 degrees of freedom are allowed in the denominator for the critical values of F distribution.

### d) Tables of Average Errors for the Individual Ion Concentrations

Tables of Average Errors are also given separately for the measurements made at the high ion concentrations and those at the low ion concentrations.

### e) Graphs of Distribution of Fractional Factorial Test Results

Graphs of the results of the fractional factorial tests were prepared by plotting ring oven value versus percentage of the total results obtained at that value. Two graphs were prepared for each set of data, one at each of the two nominal ion concentrations tested. These graphs do not show the effects due to the other five factors tested. This should be taken into consideration when evaluating the graphs.

In interpreting the results, it should be noted that a great many hypotheses are being tested, and some spurious results would be expected. If there is only one chance in twenty of finding an effect when there is really none (corresponding to a 0.05 level test), then if 20 independent tests are performed, we might expect a spurious result. The tests performed were not independent, so the relationships are somewhat more complicated. A more rigorous justification of the statistical analysis is given in Appendix B.

## 4.4 Qualifications Testing

The qualifications tests were designed to provide estimates of the following:

a) Accuracy of the ring oven procedure.
b) Precision (repeatability) of the ring oven procedure.
c) Variability due to different operators.

Using natural water samples obtained from five different sources, each of three operators made two measurements on each natural water sample at each of the ion concentration levels prescribed for that particular ion. For each ion concentration level there were a total of 30 measurements. If we let "k" denote the number of ion concentration levels for a particular ion, there were a total of 30 k measurements.

Four concentration levels were selected for each ion, as seen in Table 7 (p. 19). For a given ion, bottles were prepared for each of the five natural water samples at each of the prescribed ion concentration levels. In order to avoid the possibility that the operators had any advance knowledge as to the ion concentration level, the bottles were dispensed to the operators in a random fashion. Using a computer program, tables were generated which gave random assignments of water sample and ion level. Figure 1 shows a sample randomization chart.

In addition, fifteen blank samples were analyzed for each of the ions. These blank samples, which were not a part of the statistical matrix, were designed in order to uncover any tendencies for the test to give false positives. A false positive was considered to be significant if it were equal to or greater than the decision concentration for the particular ion. Although a blank sample should theoretically produce no color in the ring zone, this was not always the case due to background ion levels in reagents and filter paper. In some cases, however, no color was present in the ring when blank samples were run. Operators were asked to give a numerical value to blank samples whenever possible.

### 4.4.1 Selection of Natural Water Types for Qualifications Testing

Atlantic Research selected five natural water types for use in the qualifications testing, using as a guide USAMEERU Report No. 73-03 (4). These natural water types are described below:

| Water Sample | Ion Parameter Levels | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | 4 | |
| 1 | 6 | 20 | 25 | 8 | 31 | 30 | 33 | 29 |
| 2 | 18 | 39 | 4 | 17 | 34 | 10 | 32 | 24 |
| 3 | 5 | 3 | 2 | 23 | 38 | 16 | 37 | 28 |
| 4 | 35 | 26 | 22 | 27 | 14 | 36 | 7 | 12 |
| 5 | 19 | 1 | 15 | 21 | 9 | 13 | 40 | 11 |

| Sample Number | Water Sample | Ion Concentration Parameter |
|---|---|---|
| 1 | 5 | 1 |
| 2 | 3 | 2 |
| 3 | 3 | 1 |
| 4 | 2 | 2 |
| 5 | 3 | 1 |
| 6 | 1 | 1 |
| 7 | 4 | 4 |
| 8 | 1 | 2 |
| 9 | 5 | 3 |
| 10 | 2 | 3 |
| 11 | 5 | 4 |
| 12 | 4 | 4 |
| 13 | 5 | 3 |
| 14 | 4 | 3 |
| 15 | 5 | 2 |
| 16 | 3 | 3 |
| 17 | 2 | 2 |
| 18 | 2 | 1 |
| 19 | 5 | 1 |
| 20 | 1 | 1 |
| 21 | 5 | 2 |
| 22 | 4 | 2 |
| 23 | 3 | 2 |
| 24 | 2 | 4 |
| 25 | 1 | 2 |
| 27 | 4 | 1 |
| 27 | 4 | 2 |
| 28 | 3 | 4 |
| 29 | 1 | 4 |
| 30 | 1 | 3 |
| 31 | 1 | 3 |
| 32 | 2 | 4 |
| 33 | 1 | 4 |
| 34 | 2 | 3 |
| 35 | 4 | 1 |
| 36 | 4 | 3 |
| 37 | 3 | 4 |
| 38 | 3 | 3 |
| 39 | 2 | 1 |
| 40 | 5 | 4 |

Figure 1. Sample Randomization Chart

(1) Colored water - This natural water was to contain between 50 and 100 standard units of true color.

(2) Turbid water - The turbidity was to fall in the 100 to 200 JTU range, with total dissolved solids less than 500 mg/l.

(3) High total dissolved solids water - Water with a TDS of approximately 1500 mg/l was to be used, with bicarbonate as the dominant anion.

(4) Organically polluted water - This was to be water discharged before chlorination from secondary treatment at an appropriate sewage treatment plant, mixed in a 1:3 ratio with deionized water, to simulate water polluted by domestic waste.

(5) Interference water - This water was to contain elements that frequently interfere in the test procedures.

For testing the ring oven procedures, it was felt that a water of the number (5) type would be redundant, as all four of the other types should contain potential ring oven interferences. Therefore, a well water type was substituted for the interference water. The Bull Run Pond, which is used as a polishing pond after treatment at the Lower Potomac Wastewater Treatment Plant, was used as the sample for high color. The plant operator reported that the color in this pond was due to both organic matter (an aerator in the pond promoted algae growth) and to metal ions (ferric chloride was used in the treatment of water in the pond, and the water also contains zinc, copper and mercury). Bull Run Marina was chosen to represent turbid water. This site was sampled immediately after a heavy rain, in order to insure high turbidity. A well water was chosen for the high total dissolved solids water, as it was believed that dissolved minerals would be present at a high level, as the area's water is, in general, hard.

### 4.4.2 Initial Analysis of Natural Water by Standard Methods

Standard methods for the analysis of the ten ions of interest were selected and submitted to the Army for approval. These methods, which are summarized in Table 12, were taken from EPA's Methods for Chemical Analysis of Water and Wastes(5) and from Standard Methods for the Examination of Water and Wastewater.(3) All methods were approved for use.

Table 13 shows the sampling sites used to obtain the natural waters for the qualifications testing. Twenty liter samples of each water type were collected in glass carboys. Each sample was stored in a cool area, and each was bubbled slowly with air to prevent anaerobic degradation.

The data in Tables 14 and 15 show the results of the physical and chemical analyses of the water samples. The samples were not analyzed for lead at a greater sensitivity, because this ion was later dropped from the qualifications testing.

In order to fulfill the requirements for the various water types, as discussed in Section 4.4.1, some adjustment of various physical properties was required. Turbidity and color were augmented in the same manner as used in the ruggedness tests (with kaolin and food coloring). A high total dissolved solids level was attained by addition of solid sodium carbonate and sodium bicarbonate to the bulk water sample. This resulted in a buffering effect for this particular natural water sample.

It was decided that samples for both qualifications testing and fractional factorial testing which contained turbid matter would be filtered, rather than digested, prior to analysis, since in most field situations the water would be filtered prior to human consumption. It was discovered during preliminary testing that the turbid matter caused erroneous results due to dissolution of metals from the turbid matter by acid wash solutions.

### 4.4.3 Preparation of Samples for Qualifications Testing

The values obtained in the analysis of the natural waters (Tables 14 and 15) were used to calculate the amount of primary standard solution needed to bring the natural water samples up to a predetermined ion concentration. The correct amount of the primary standard was then added to the appropriate volume of natural water sample. These spiked samples were not subjected to further analysis to determine ion content by standard

TABLE 12. Analytical Methods Summary Sheet

| Ion | Method | Reference |
|---|---|---|
| Iron | AA-$C_2H_2$, air | Storet No. 01045, EPA, p. 110 |
| Zinc | AA-$C_2H_2$, air | Storet No. 01092, EPA, p. 155 |
| Mg | AA-$C_2H_2$, air (La required) | Storet No. 00927, EPA, p. 114 |
| Pb | AA-$C_2H_2$, air<br>(extraction recommended <0.01 ppm) | Storet No. 01051, EPA, p. 112 |
| Cu | AA-$C_2H_2$, air | Storet No. 01042, EPA, p. 108 |
| Ca | AA-$C_2H_2$, air<br>(La corrects for interferences) | Storet No. 00916, EPA, p. 103 |
| $NO_3$ | Chromotropic acid | Standard Methods of Water and Wastewater, p. 429 |
| F | Specific ion electrode | Storet No. 00951, EPA, p. 65 |
| Cl | $HgNO_3$ titration | EPA, p. 29; Standard Methods, p. 304 |
| $SO_4$ | Turbidimetric | EPA, p. 277, Standard Methods, p. 496 |

TABLE 13. Sampling Locations, Natural Water Samples

| Sample Type | Sampling Locale |
|---|---|
| Colored | Bull Run Pond, Lower Potomac Wastewater Treatment Plant |
| Turbid Water | Bull Run Marina |
| Organically Polluted Water | Secondary Effluent, Lower Potomac Wastewater Treatment Plant (Diluted 1:3 with deionized water) |
| High Total Dissolved Solids Water | Vienna, Virginia, well (spiked with sodium carbonate and sodium bicarbonate) |
| Well Water | Vienna, Virginia, well (unspiked) |

TABLE 14. Ion Analysis (ppm) of Natural Water Samples*

| Ion | Turbid | Colored | Well | High TDS | Organically Polluted |
|---|---|---|---|---|---|
| Zn | <0.02 | 0.061 | 0.071 | <0.02 | 0.057 |
| Fe | <0.0216 | 0.12 | 0.026 | <0.026 | 0.030 |
| Ca | 36.4 | 26.6 | 3.90 | 12.7 | 8.90 |
| Mg | 9.44 | 6.18 | 2.65 | 2.94 | 1.42 |
| Cu | <0.019 | 0.250 | 0.036 | 0.156 | <0.019 |
| F | 0.270 | 1.06 | 0.034 | 0.043 | 0.219 |
| Cl | 14.67 | 30.4 | 12.67 | 12.14 | 5.18 |
| $SO_4$ | 8.25 | 46.5 | 1.3 | 2.1 | 7.1 |
| $NO_3$ | 1.88 | 6.25 | 2.4 | 1.25 | 1.25 |
| Pb | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |

*These samples were spiked when necessary, in order to bring turbidity, color and TDS within limits.

Table 15. Physical Properties of Natural Water Samples*

| | Turbid | Colored | Well | High TDS | Organically Polluted |
|---|---|---|---|---|---|
| pH | 7.71 | 5.49 | 6.79 | 8.98 | 7.65 |
| Turbidity (JTU) | 200 | 9.8 | 4.6 | 1.4 | 4.6 |
| Color (Standard Color Units) | 15 | 100 | 2 | 20 | 7 |
| TDS (mg/l) | 5.6 | 572 | 226 | 1110 | 364 |

*These samples were spiked when necessary in order to bring turbidity, color, and TDS within limits.

methods. Blank samples consisted of deionized water. All samples were placed in acid-washed polyethylene bottles numbered randomly.

### 4.4.4 Treatment of the Results of the Qualifications Tests

For each of five water samples, three operators made two measurements at each of four ion concentrations for a total of 120 measurements for each ion. The order in which the measurements were made was randomized.

The set of all measurements was in the form of a complete 5 by 3 by 4 factorial design with two replications. In the analysis, the different water samples were considered to be a fixed effect, since they represented distinct types of water. The ion concentrations were also considered a fixed effect, but the operators were considered a random effect. The actual ion concentration was subtracted from each measurement, so the analysis was performed on the errors of the measurements. The results of the analysis are given in a series of tables in Section 5.0 for each of the ions considered.

#### a) Overall Analysis of Variance Tables

An analysis of variance was performed using all of the data for each ion. The results are given in the analysis of variance tables in Section 5.0. The analysis was performed for the operator, ion concentration, water sample type factors and their first order interactions. In the tables in Section 5.0, the letter X (read cross) separates the two factors in each interaction. Thus OP X ION LEV means the interaction between operator and ion level. The sum of squares (SS) for each factor was that part of the total sum of squares which was attributable to that factor. The mean square (MS) was obtained by dividing the sum of squares by degrees of freedom. The values of F were calculated as ratios of mean squares. In each case, the numerator was the mean square for that factor. For operator, and for three interactions, the denominator was the precision mean square. For ion concentration, the denominator was the mean square for the operator-ion concentration interaction, and for water sample, the denominator was the mean square for the operator-water sample interaction.

A large value for F indicated that the corresponding factor has a significant effect (on measurement accuracy). In order to determine whether a factor had a significant effect, the calculated F value was compared to a table of critical values for the F distribution. (The degrees of freedom for numerator and for denominator were those for the mean squares in the numerator and denominator of the F ratio.) If the calculated F value exceeds the critical value for a given significance level, then the factor was judged significant at that level. (Note that the critical values depend also upon the numerator and denominator degrees of freedom.) Following the F value, a single asterisk (*) means it was significant at the 0.05 level, but not at the 0.01 level; two asterisks (**) signify that it was significant at the 0.01 level, in which case it was considered highly significant.

b) <u>Tables of Average Errors of Measurement</u>

Tables are presented in Section 5.0 which give the average errors of measurements for different levels of two of the three factors, and also average errors for the different levels of the factors taken individually. For instance, for the zinc ion (Section 5.0, page 81) it may be seen that, for the second operator, the average error (averaged over all water samples) of all measurements made at ion level 10 was -2.70, and that the average error for Operator 2 for all measurements made on Water Sample 2 was -0.25. Also, the average error for all measurements at ion level 10 was -1.233. In each case, the error value is the measured ion level minus actual ion level.

c) <u>Estimates for Precision and Operator Variability</u>

Estimates are also given in Section 5.0 for the precision of the measurements and for the operator variability. The precision was estimated:

$$S_p^2 = \Sigma(Y_{ijkl} - Y_{ijkl})^2/120$$

and measured the variation in repeated measurements of the same sample by a single operator.

The operator variability was estimated by:

$$S_o^2 = \frac{\text{Operator Mean Square - Precision Mean Square}}{40}$$

where Operator Mean Square and Precision Mean Square are given in the Analysis of Variance Table.

### d) Analysis of Variance for Individual Ion Concentration Tables

Since the results seemed to vary with the different ion concentrations, a separate analysis of variance was performed for each ion concentration. The value for $S_p^2$ was given with each table and, if the operator effect was significant, the value for $S_o^2$ was also given. The equations for determining $S_p^2$ and $S_o^2$ were the same as in (c) above, except that in each case the denominator was divided by 4.

### e) Use of the Ring Oven Procedure as a Screening Device

In addition to the above analyses, the potential usefulness of the ring oven procedure as a screening device was also considered. For each ion, four standards were selected, one of which was the decision concentration. If the ion concentration was above the decision concentration, presumably the water would not be used. Of the ion concentrations used in the individual experiments, two were above the decision concentration and two were below. If the ring oven procedure was to be considered as a screening device, then the only determination of interest would be whether the ion concentration was above or below the decision concentration. One might consider different strategies for using the ring oven results for screening. A procedure that might work reasonably well would be as follows. The operator makes two measurements. If both are above the decision concentration, it would be concluded that the ion concentration was above the critical level. If both were below the decision concentration, it would be concluded that the ion concentration was below the critical level. If one measurement was above the critical level and one measurement was below the critical level, additional measurements would be necessary. Ideally, such a procedure would leave room for few mistakes, particularly if the actual ion concentration is far from the critical level.

This procedure was tested for each ion using the data for these experiments. For several reasons the results must be regarded as only tentative for reasons noted below.

1) In the experiments, the order in which measurements were made was randomized over the various ion levels and repetitions of measurements. Thus when the operator made the second measurement at a particular combination of water sample and ion concentration, he was unaware of the result of his first measurement. In the field, the operator would know the result of his first measurement when he made the second measurement. This could result in a bias toward the second measurement. It could also lead to a re-examination of the measurements if the results were widely different, or could result in making an additional measurement.
2) The measurements were made in a laboratory and not in the field.
3) Since only two measurements were made by an operator, it was not at all clear what the result would be if, knowing those results, he made additional measurements (presumably more carefully).
4) A number of measurements were made at the critical level (which was one of the standards) If the criterion was both above or both below, then the operator would presumably try to determine whether it was actually slightly above or below.

In addition, graphical representations of the results of the general screening analysis are presented. These bar graphs, which can be found in Section 5.0, related to the number of correct "go-no go" decisions made at each ion concentration for each ion. The following criteria were used in preparing these figures:

- A sample was considered to contain an unacceptable ion concentration if the ion concentration was equal to or greater than the decision concentration.

- A sample was considered to warrant a "go" decision if the ion concentration was less than the decision concentration.
- Thirty samples were run at each concentration for a total of 120 samples.
- Results diagrammed in the figures in Section 5.0 are those obtained in the qualifications tests only.

### 4.5 Types of Operators Used During Statistical Evaluation Tests

Attempts were made to use operators of widely varying educational and technical experience in order to test the ring oven in a manner which was as realistic as possible. Table 16 gives a brief description of the background of the operators used. Operators were not varied during a single phase of testing of an ion; that is, the same three operators performed all of the qualifications tests for copper, and so on. The numbers used to designate each operator in Table 16 do not necessarily refer to the designating numbers of the operators who performed a test as given in Section 5.0.

Little difference was noticed among operators according to educational level or previous ring oven experience. This demonstrates the simplicity of operation of the ring oven/spot test technique.

### 4.6 General Ion Schemes

In addition to qualifications testing and fractional factorial testing of the procedures developed under Contract DADA17-73-C-3112, it was thought that it would be desirable to develop general screening methods that would indicate the presence of a large number of ions with one reagent. A procedure using such a reagent would save analysis time by eliminating the need to examine a sample for each ion of interest individually unless the general scan showed a total ion concentration level above a predetermined threshold limit. Ideally, the sample would be applied, washed to the ring zone with an acid or buffer (metals) or with deionized water, and the reagent applied.

The intensity of the resulting rings would then be compared to standards consisting of rings of equal intensity containing varying known

## TABLE 16. Operators Used in Ring Oven Testing

| Operator No. | Educational Professional Experience | Previous Ring Oven Experience |
|---|---|---|
| 1 | Sergeant/USAMERDC; involved in water quality | None |
| 2 | Masters Degree in civil engineering/USAMERDC | None |
| 3 | Some college; chemical technician/ARC | 4 months |
| 4 | Some college; junior technician, part-time/ARC | 4 months |
| 5 | Technical typist/ARC | None |
| 6 | Some college; Junior technician/ARC | None |
| 7 | Bachelor's Degree in English; part-time technician/ARC | None |
| 8 | Two years' college chemistry; chemical technician/ARC | None |

amounts of ions. For example, a ring of intensity A is compared to standard rings, also of intensity A. These standards might contain 0.1 μg iron, 2 μg lead, and 2 μg zinc respectively. One could then say that the unknown ring of intensity A contained no more than 0.1 μg Fe, 2 μg Pb and 2 μg Zn.

A question arose as to the effect of various ring colors from different ions on intensity readings. Especially in the cases of the metals, one reagent will usually produce a different color with each individual ion. In order to circumvent this problem, the use of black-and-white standard photographs was found to be an effective means of neutralizing the contrasting color possibilities.

General ion scan tests were performed by depositing a known amount of a specific ion in the ring zone, treating it with the screening reagent and comparing its intensity to that of other ions similarly prepared using the identical screening reagent. Rings of equivalent intensities, but not necessarily the same color, were then grouped and photographed in black-and-white in order to compare their photographic contrast. The results of these studies are described in Section 5.2.

## 4.7 Evaluation of Ring Oven/Spot Test Techniques for Monitoring Pesticides in Water

The proliferation of pesticides throughout our environment has induced serious concern with respect to health hazards in recent years. Of particular importance in connection with this problem is the fate of the earth's water supplies.

As discussed previously, the Army's requirements for water test kits center around the need for decisions concerning water supply potability. It can be seen that the criteria upon which such decisions are based are highly dependent upon the ways in which the water will be utilized. For example, if the water is to be consumed over a long period of time, it is important that the most stringent standards be met with respect to safe concentrations. The National Academy of Sciences, in conjunction with the National Academy of Engineering, have set such standards for the pesticides in surface water in their report, "Water Quality Criteria," March, 1973. These standards were selected by the Army for use in ring oven feasibility studies and are shown, along with the concentration range required by the Army, in Table 17.

TABLE 17. Pesticide Limits for Ring Oven Feasibility Studies

| Pesticide | Detection Limit (ppm) | Concentration Range Required (ppm) |
|---|---|---|
| Organophosphorus | 0.01 | 0.01 - 4.0 |
| Organochlorine (dieldrin) | 0.001 | 0.001 - 2.0 |
| Arsenical (as As) | 0.1 | 0.1 - 5.0 |
| Cyanide | 0.2 | 0.2 - 40.0 |

In the case of pesticides, the possibility of short term consumption of water supplies must be considered. It is probable that in certain situations, such as in a battlefield environment, only one water supply may be available. This may require a lowering of water quality standards if safety factors can still be met for a short period of time.

Another aspect of water quality of particular military concern is the threat of sabotage. Again, this is of very great importance when only one water supply is available. It appears likely that such readily obtainable and highly toxic chemicals as pesticides would be prime candidates for use in sabotage of water supplies. When evaluating and selecting suitable field monitoring methods for pesticides in water, then, one should consider the uses to which the water will be put. The sensitivity required for any field monitoring technique will be dependent upon whether long-term or short-term consumption is intended, or whether massive contamination must be detected.

The ring oven seemed to offer promise as a method of monitoring pesitcides in natural waters in a field situation. One chemical was selected to represent each of four classes of pesticide during ring oven feasibility testing. These chemicals are given in Table 18. Several criteria were used in selection of pesticides. Low toxicity dosage coupled with low volatility were to provide a good safety factor for the ring oven operators during laboratory testing. A relatively high water solubility was also desired in order to insure initial high values for preliminary reagent scans.

Table 18. Selected Pesticides for Ring Oven Feasibility Studies

| Pesticide Class | Pesticide Selected |
|---|---|
| Arsenical | Methanearsonic acid, disodium salt (DSMA) |
| Cyanide | Sodium cyanide |
| Organochlorine | Dieldrin |
| Organophosphorus | Malathion |

Pesticide standards were prepared for dieldrin (200 ppm in benzene), malathion (138 ppm in benzene), arsenic (100 ppm As as disodium methyl arsenate), and cyanide (1000 ppm $CN^-$ as sodium cyanide). Benzene was used as the solvent for the organochlorine and organophosphorus compounds so that solutions of a sufficiently high concentration for preliminary reagent scanning could be prepared. The standards were kept refrigerated.

Feasibility studies were performed by depositing varied amounts of the pesticide in the ring zone, treating with reagent, and comparing intensities. The results of the feasibility studies for pesticides are given in Section 5.3.

# 5.0 RESULTS AND DISCUSSION

## 5.1 Statistical Evaluation of the Ring Oven Method

The following section documents the results of the statistical evaluation of the ring oven method for copper, calcium, magnesium, zinc, iron, lead, nitrate, fluoride, chloride, and sulfate. Included are discussions and data obtained from the operator variability tests, fractional factorial tests, qualifications tests, and blank tests for these ten ions. Ring oven procedures for each ion used for the laboratory statistical studies are given in Appendix C. More detailed information as to the development of the reagents and procedures tested can be found in Reference (1).

Several factors must be considered in evaluation of test results. The nature of the tests required the operators to make a great number of repetitive measurements (up to 55 for the qualifications tests) following a single procedure. Within a procedure, multiple applications of sample were frequently necessary. It is very easy to forget how many applications have been made, unless extremely close attention is paid to the operation. Likewise, during quantitation of a great number of rings, a tendency exists for all rings to look alike after a period of time. It must also be recognized that samples spiked with various amounts of the particular ions were not analyzed for ion content after the spiking, due to time constraints. Therefore, ion concentrations were only nominal and errors obtained may have been due to errrors in producing test samples.

### 5.1.1 Copper

The reagent selected, dithiooxamide, was originally evaluated over the range of 0.1 to 5.0 ppm, with standard values of Blank, 0.1, 0.5, 1.0, 2.5, and 5.0 ppm.

#### Procedure Adjustment

During the initial operator variability testing, it was observed that some of the more inexperienced operators were having difficulty in forming rings using the 3M ammonium hydroxide solution. This difficulty disappeared as the ammonium hydroxide solutions aged. As no appreciable change in concentration was seen between new and aged ammonium solution, it was thought that a possible change in carbon dioxide content of the solution might prove to be causing the difference in ease of ring formation. For this reason, then, the wash solution was changed to include one gram of solid ammonium carbonate in every 100 ml of 3M $NH_4OH$. Use of this wash solution proved to be successful. The procedure used in all subsequent copper analyses is shown in Appendix C.

Dithiooxamide is also sensitive to cobalt and nickel ions under the conditions used in the ring oven test. The metals iron, silver, bismuth, mercury, palladium and platinum, which ordinarily react with dithiooxamide, are precipitated in the center of the filter paper by the ammonium hydroxide-ammonium carbonate solution. For a more detailed discussion of the interferences and their elimination for the dithiooxamide-copper test, see Reference (1).

### Operator Variability Tests

Initial standard values tested during this study for copper were 0.5, 1, 2, and 4 ppm. The results of tests with these standard rings are given in Table 19. As can be seen from these data, results are low, almost without exception. Run No. 2 for copper, which is given in Table 20, was performed using standards of 0.1, 1, 4, and 8 ppm. Results were still showing a tendency to be low.

One possible explanation for these low readings was thought to be difference in experience between the operators and the project chemist who prepared the standards. For this reason, a run was made in which operator No. 3 prepared the standard rings for Operator No. 4 and vice versa. The rings from Run No. 2 were compared to operator-generated standards. The results of this test are given in Table 21. On the average, the results were erratic, especially at 1 ppm or less. Differences in experience did not seem to be the cause of this erratic tendency; however, it must be recognized that both operators in this test had some ring oven experience.

TABLE 19. Operator Variability Tests - Copper, Run No. 1

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No.3 (ppm) | Ring Oven Results Operator No. 4 (ppm) |
|---|---|---|---|
| A | Blank | >4.0 | Blank |
| B | 1.0 | 1.0 | 0.5 |
| C | 0.5 | <0.5 | 0.5 |
| D | 4.0 | 4.0 | 4.0 |
| E | 0.5 | <0.5 | 0.5 |
| F | 4 | <0.5 | 2 |
| G | 1.0 | <0.5 | 0.5 |
| H | 2.0 | 1.0 | 1.0 |
| I | 4.0 | 2.0 | 0.7 |
| J | 2.0 | 1.0 | 0.5 |
| K | 1.0 | <0.5 | 0.5 |
| L | 2.0 | 1.0 | 2.0 |
| M | 4.0 | 2.0 | 4.0 |
| N | 0.5 | 0.5 | 0.5 |
| O | 1.0 | 0.5 | 0.5 |
| P | 0.5 | <0.5 | <0.5 |
| Q | 4.0 | 2.0 | 4.0 |
| R | 2.0 | 2.0 | 0.5 |
| S | 2.0 | 1.0 | <0.5 |
| T | 1.0 | <0.5 | <0.5 |

50 µl Samples

Standards: 0.5-1-2-4

Decision Level: 1 ppm

**TABLE 20.** Operator Variability Tests - Copper, Run No. 2

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No.3 (ppm) | Ring Oven Results Operator No. 4 (ppm) |
|---|---|---|---|
| A | Blank | <0.1 | 0.1 |
| B | 1.0 | <0.1 | 1.0 |
| C | 0.5 | 0.1 | 0.5 |
| D | 4.0 | 2.0 | 3.0 |
| E | 0.5 | 2.0 | 0.7 |
| F | 4.0 | 1.0 | 4.0 |
| G | 1.0 | 0.1 | 0.9 |
| H | 2.0 | <0.1 | 2.0 |
| I | 4.0 | 1.0 | 2.0 |
| J | 2.0 | 0.1 | 0.9 |
| K | 1.0 | 0.1 | 0.5 |
| L | 2.0 | 0.5 | 0.9 |
| M | 4.0 | <1.0 | 1.0 |
| N | 0.5 | 0.1 | 0.2 |
| O | 1.0 | 0.1 | 0.2 |
| P | 0.5 | <0.1 | 0.1 |
| Q | 4.0 | 1.0 | 1.0 |
| R | 2.0 | 0.1 | 0.9 |
| S | 2.0 | 1.0 | 1.0 |
| T | 1.0 | 0.1 | 0.1 |
| U | 8.0 | 4.0 | 3.0 |
| V | 8.0 | 1.0 | 4.0 |
| W | 0.1 | <0.1 | 0.5 |
| X | 0.1 | <0.1 | 0.1 |
| Y | 8.0 | 4.0 | 7.0 |

50 µl Samples

Standards: 0.1-1-4-8

Decision Level: 1 ppm

TABLE 21. Operator Variability Tests - Copper, Run No. 2a

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 3 Stnds by Operator No. 4 (ppm) | Ring Oven Results Operator No. 4 Stnds by Operator No.3 (ppm) |
|---|---|---|---|
| A | Blank | 0.1 | 0.1 |
| B | 1.0 | 0.1 | 2.0 |
| C | 0.5 | 0.5 | 1.0 |
| D | 4.0 | 4.0 | 4.0 |
| E | 0.5 | 8.0 | 0.7 |
| F | 4.0 | 8.0 | 0.4 |
| G | 1.0 | 0.8 | 1.0 |
| H | 2.0 | 1.0 | 3.0 |
| I | 4.0 | 8.0 | 4.0 |
| J | 2.0 | 0.7 | 2.0 |
| K | 1.0 | 0.5 | 0.2 |
| L | 2.0 | 1.0 | 2.0 |
| M | 4.0 | 0.1 | 4.0 |
| N | 0.5 | 0.1 | 0.2 |
| O | 1.0 | 0.5 | 0.1 |
| P | 0.5 | <0.1 | 0.1 |
| Q | 4.0 | 4.0 | 1.0 |
| R | 2.0 | 0.3 | 0.7 |
| S | 2.0 | 4.0 | 0.5 |
| T | 1.0 | 0.5 | 0.1 |
| U | 8.0 | 8.0 | 5.0 |
| V | 8.0 | 5.0 | 8.0 |
| W | 0.1 | <0.1 | 0.5 |
| X | 0.1 | 0.1 | 0.1 |
| Y | 8.0 | 8.0 | 9.0 |

50 μl Samples

Standards: 0.1-1-5-8

Decision Level: 1 ppm

As low analysis values had previously been encountered due to copper adsorption and biological action, it was decided to prepare fresh synthetic water samples. An analysis of these samples by one operator, as shown in Table 22, proved successful. Tests were then performed using two operators and fresh samples. Table 23 gives the results. It would appear that results for Sample A, which was thought to contain "8", but for which both operators read "4" in repeated analyses, was an incorrectly prepared sample. Unfortunately, time was not available for an atomic absorption analysis to substantiate the actual concentration.

At the request of the Army, Atlantic Research performed some further limited investigations of the first four copper standards (0.5, 1, 2, and 4 ppm). After this limited investigation, which consisted of preparation of multiple sets of standards and comparison of the gradations of equivalent standards of different sets, it was decided that using 0.5, 1, 2, and 4 ppm copper as permanent standard values sufficiently encompassed any operator variability.

## Fractional Factorial Tests

The results of the fractional factorial tests for the copper ion are presented in Table 24 and shown graphically in Figure 2. Tables 25a, 25b and 25c give the statistical analyses of the results, while Table 26 summarizes the various effects.

As can be seen from Table 25a for all observations, there is a highly significant interaction between factors 2 and 3, color and reagent temperature (indicated by a double star). This interaction, which is also confirmed as being significant by the alternate analysis using all higher order interactions in Table 25 b is only critical at the higher ion concentration.

On the other hand, a significant effect is shown by turbidity and color interactions at the high ion concentration, and by detection reagent temperature and chlorine concentration at the low level, indicated by a single star. The 0.75 ppm value obtained for sample r (nominal value = 3 ppm) may be due to the first of the two interactions.

Table 22. Operator Variability Tests - Copper, Run No. 3, Fresh Sample

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 4 (ppm) |
|---|---|---|
| A | 8.0 | 8.0 |
| B | 1.0 | 0.9 |
| C | 4.0 | 4.0 |
| D | 4.0 | 4.0 |
| E | 1.0 | 1.0 |
| F | 8.0 | 8.0 |
| G | 0.1 | 0.1 |
| H | 0.1 | 0.5 |
| I | 0 | 1.0 |
| J | 0.1 | 0.1 |
| K | 1.0 | 1.0 |
| L | 4.0 | 4.0 |
| M | 1.0 | 1.0 |
| N | 4.0 | 6.0 |
| O | 1.0 | 1.0 |
| P | 8.0 | 8.0 |

50 μl Samples

Standards: 0.1-1-4-8

Decision Level: 1 ppm

TABLE 23. Operator Variability Tests - Copper, Run No. 4

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| A | 8.0 | 4.0 (4.0)* | 4.0 (4.0) |
| B | 1.0 | 1.0 | 0.5 |
| C | 4.0 | 4.0 | 3.0 |
| D | 4.0 | 4.0 | 3.0 |
| F | 8.0 | 5.0 | 7.0 |
| G | 0.1 | <0.1 | 0.1 |
| H | 0.1 | <0.1 | <0.1 |
| I | Blank | <0.1 | <0.1 |
| J | 0.1 | 0.1 | <0.1 |
| L | 4.0 | 3.0 | 2.0 |
| N | 4.0 | 3.0 (3.0) | 1.0 (3.0) |
| P | 8.0 | 6.0 | 6.0 |
| Q | 1.0 | 1.0 | 0.6 |
| R | 1.0 | 0.9 | 0.9 |
| S | 1.0 | 1.0 | 1.0 |
| T | 4.0 | 3.0 | 3.0 |

50 µl Samples

Standards: 0.1-1-4-8

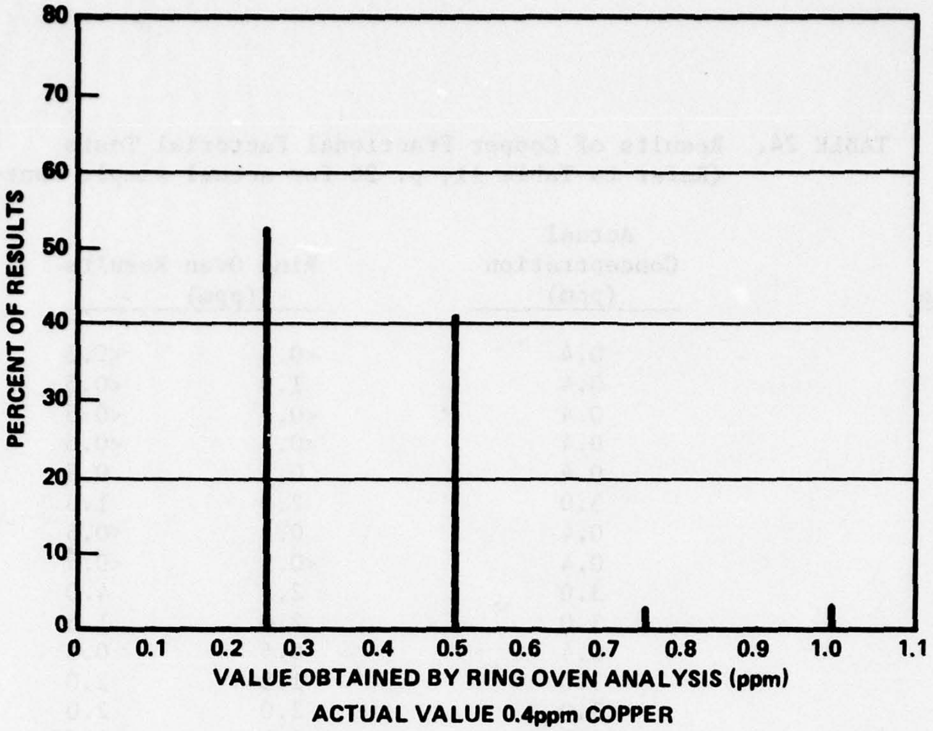
Decision level: 1ppm

*Numbers in parenthesis represent repeat analysis.

TABLE 24. Results of Copper Fractional Factorial Tests
(Refer to Table 11, p. 26 for actual sample content)

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 0.4 | <0.5 | <0.5 |
| b | 0.4 | 1.0 | <0.5 |
| c | 0.4 | <0.5 | <0.5 |
| d | 0.4 | <0.5 | <0.5 |
| e | 0.4 | 0.5 | 0.5 |
| f | 3.0 | 2.0 | 1.5 |
| g | 0.4 | 0.5 | <0.5 |
| h | 0.4 | <0.5 | <0.5 |
| i | 3.0 | 2.5 | 4.0 |
| j | 3.0 | 2.0 | 1.5 |
| k | 0.4 | 0.5 | 0.5 |
| l | 3.0 | 1.5 | 2.0 |
| m | 3.0 | 2.0 | 2.0 |
| n | 0.4 | 0.5 | 0.75 |
| o | 0.4 | 0.5 | 0.5 |
| p | 3.0 | 3.0 | 2.0 |
| q | 0.4 | 0.5 | 0.5 |
| r | 3.0 | 0.75 | 3.0 |
| s | 3.0 | 3.0 | 3.0 |
| t | 3.0 | 1.0 | 1.5 |
| u | 0.4 | <0.5 | <0.5 |
| v | 0.4 | <0.5 | <0.5 |
| w | 3.0 | 2.0 | 2.0 |
| x | 0.4 | <0.5 | <0.5 |
| y | 3.0 | 1.0 | 1.0 |
| z | 0.4 | <0.5 | 0.5 |
| aa | 3.0 | 1.0 | 2.0 |
| bb | 0.4 | 0.5 | 0.5 |
| cc | 3.0 | 1.0 | 2.0 |
| dd | 3.0 | 1.5 | 4.0 |
| ee | 3.0 | 2.0 | 4.0 |
| ff | 3.0 | 1.0 | 2.0 |

**Standards:** 0.5 - 1 - 2 - 4
Operator No. 4



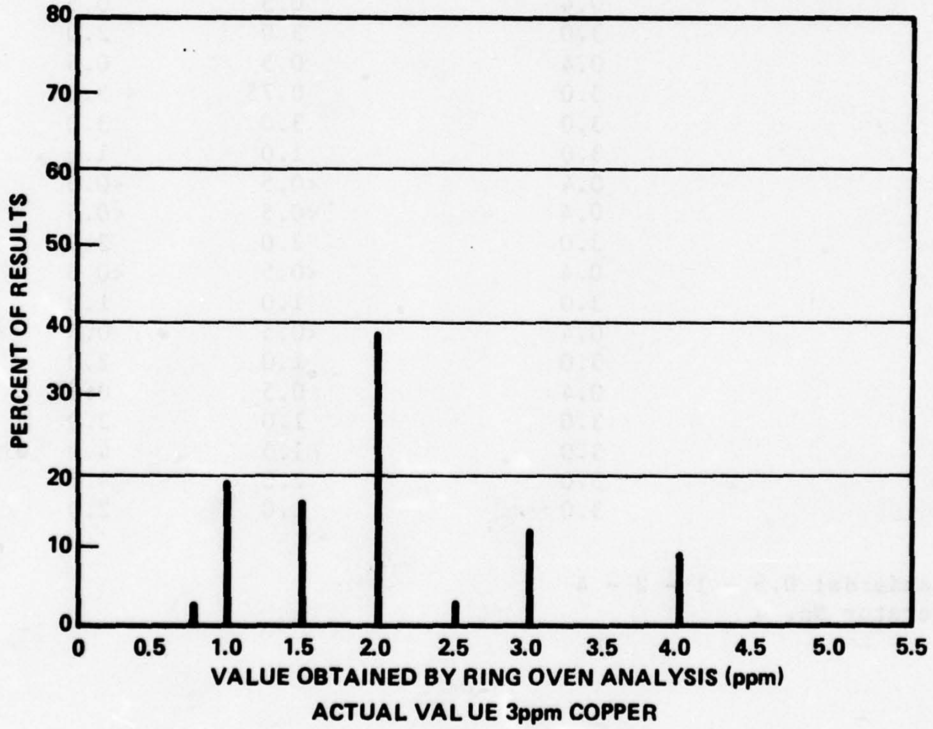


Figure 2. Percent Distribution of Copper Fractional Factorial Test Results at Tested Ion Concentrations

### TABLE 25(a). Statistical Analysis of Copper Fractional Factorial Tests

$S_p^2/2$ used for residual mean square

Analysis of Variance

| All Observations | | | High Ion Concentration | | | Low Ion Concentration | | |
|---|---|---|---|---|---|---|---|---|
| **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** |
| 1 | 0.00 | 0.00 | 1 | 0.00 | 0.00 | 1 | 0.00 | 0.33 |
| 2 | 0.14 | 0.77 | 2 | 0.28 | 0.80 | 2 | 0.00 | 0.00 |
| 3 | 0.67 | 3.67 | 3 | 0.82 | 2.33 | 3 | 0.06 | 5.33* |
| 4 | 0.00 | 0.00 | 4 | 0.01 | 0.02 | 4 | 0.00 | 0.33 |
| 5 | 0.11 | 0.60 | 5 | 0.02 | 0.07 | 5 | 0.10 | 8.33* |
| 6 | 7.48 | 41.09** | 12 | 0.02 | 0.07 | 12 | 0.00 | 0.00 |
| 12 | 0.67 | 3.67 | 13 | 0.28 | 0.80 | 13 | 0.02 | 1.33 |
| 13 | 0.22 | 1.18 | 14 | 0.08 | 0.22 | 14 | 0.00 | 0.33 |
| 14 | 0.02 | 0.13 | 15 | 0.52 | 1.47 | 15 | 0.04 | 3.00 |
| 15 | 0.41 | 2.25 | 23 | 2.95 | 8.38* | 23 | 0.04 | 3.00 |
| 16 | 0.00 | 0.02 | 24 | 0.05 | 0.14 | 24 | 0.02 | 1.33 |
| 23 | 1.82 | 9.98** | 25 | 0.22 | 0.62 | 25 | 0.02 | 1.33 |
| 24 | 0.06 | 0.32 | 34 | 0.02 | 0.07 | 34 | 0.02 | 1.33 |
| 25 | 0.06 | 0.32 | 35 | 0.12 | 0.34 | 35 | 0.00 | 0.00 |
| 26 | 0.14 | 0.77 | 45 | 0.17 | 0.47 | 45 | 0.00 | 0.33 |
| 34 | 0.00 | 0.00 | | | | | | |
| 35 | 0.06 | 0.32 | | | | | | |
| 36 | 0.22 | 1.18 | | | | | | |
| 45 | 0.11 | 0.60 | | | | | | |
| 46 | 0.01 | 0.07 | | | | | | |
| 56 | 0.01 | 0.07 | | | | | | |

$S_p^2 = 0.364$ $S_p^2 = 0.705$ $S_p^2 = 0.0234$

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 25(b). Statistical Analysis of Copper Fractional Factorial Tests

### Analysis of Variance - All Observations

Residual mean Square = 0.246†

| Factor | SS | F Value |
|---|---|---|
| 1* | 0.00 | 0.00 |
| 2 | 0.14 | 0.57 |
| 3 | 0.67 | 2.72 |
| 4 | 0.00 | 0.00 |
| 5 | 0.11 | 0.45 |
| 6 | 7.48 | 30.40** |
| 12 | 0.67 | 2.72 |
| 13 | 0.22 | 0.87 |
| 14 | 0.02 | 0.10 |
| 15 | 0.41 | 1.67 |
| 16 | 0.00 | 0.02 |
| 23 | 1.82 | 7.38* |
| 24 | 0.06 | 0.24 |
| 25 | 0.06 | 0.24 |
| 26 | 0.14 | 0.57 |
| 34 | 0.00 | 0.00 |
| 35 | 0.06 | 0.24 |
| 36 | 0.22 | 0.87 |
| 45 | 0.11 | 0.45 |
| 46 | 0.01 | 0.05 |
| 56 | 0.01 | 0.05 |

†For this table, the lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

TABLE 25(c). Statistical Analysis of Copper Fractional Factorial Tests

The Average Errors for the High and Low Levels of Each Factor Are:[†]

|  | High | Low |
|---|---|---|
| 1 | -0.489 | -0.497 |
| 2 | -0.427 | -0.559 |
| 3 | -0.637 | -0.348 |
| 4 | -0.489 | -.0497 |
| 5 | -0.434 | -0.552 |
| 6 | -0.977 | -0.009 |

(For all observations)

|  | High | Low |
|---|---|---|
| 1 | -0.984 | -0.969 |
| 2 | -0.844 | -1.109 |
| 3 | -1.203 | -0.750 |
| 4 | -0.953 | -1.000 |
| 5 | -0.938 | -1.016 |

(At the high ion concentration)

|  | High | Low |
|---|---|---|
| 1 | +0.006 | -0.025 |
| 2 | -0.009 | -0.009 |
| 3 | -0.072 | +0.053 |
| 4 | -0.025 | +0.006 |
| 5 | +0.069 | -0.087 |

(At the low ion concentration)

---

[†] Measured ion concentration minus nominal ion concentration

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

TABLE 26. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Copper

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | - | - | - | - | - | - |
| Color | - | - | ** | - | - | - |
| Detection Reagent Temperature | - | ** | - | - | - | - |
| Reagent Age | - | - | - | - | - | - |
| Chlorine Concentration | - | - | - | - | - | - |
| Ion Concentration | - | - | - | - | - | ** |

- = no significant effect
* = significant effect
** = highly significant effect

Another factor shown as being highly critical for all observations is ion concentration. This is confirmed by the individual analyses performed at the high and low ion concentrations, which show both a lesser precision and a greater average error at the high ion concentration. This is probably due to the fact that at higher ion concentrations, ring intensities are darker. When a slight change in ring intensity occurs at higher concentrations, the eye has more difficulty distinguishing this change.

## Qualifications Tests

The results of the qualifications testing for copper are shown in Table 27. Table 28 presents the results of the blank tests. Figure 3 shows the permanent standards used for the copper qualifications (It was not practical at this time to reproduce sufficient copies of the permanent standards for wide distribution. Therefore, this figure and subsequent figures illustrating permanent standards appear in only four copies.)

For this ion, the standards were 0.5, 1.0, 2.0 and 4.0 ppm. The ion concentrations used were 0.4, 0.7, 1.5 and 3.0 ppm. The data are, in general, quite consistent, except for high measurements by Operator 3 at 0.7 ppm (High TDS Water) and one low measurement by Operator 3 at 3.0 ppm (Organically Polluted Water). The low measurement is probably due to failure to apply the correct amount of sample. This procedure requires three sample aliquots.

Table 29 shows the statistical evaluation of the qualifications tests. The analysis of variance shows significant effects due to the different operators and interactions of the operators with both ion concentration and water samples. The value for $S_p^2$ (the estimate of precision) is somewhat smaller than that obtained from the fractional factorial testing. The estimate of operator variability, $S_o^2$, is much smaller than $S_p^2$. The average errors at the individual ion levels do not exceed 0.16 ppm, which is excellent. The high total dissolved solids water gave greater positive error than the other four water types; this was not expected, as it would seem that a negative error would be encountered through precipitation of copper carbonate. On the other hand, the greatest negative error was

TABLE 27. Copper Qualifications Tests

Standards: 0.5 - 1.0 - 2.0 - 4.0

| Water Sample | Operator | Measurement | Ion Concentration 0.4 ppm | 0.7 ppm | 1.5 ppm | 3.0 ppm |
|---|---|---|---|---|---|---|
| Turbid | 1 | 1 | 0.5 | 0.6 | 1.9 | 3.0 |
| | | 2 | 0.2 | 0.8 | 1.0 | 3.0 |
| | 2 | 1 | 0.4 | 0.7 | 1.2 | 2.1 |
| | | 2 | 0.4 | 0.5 | 1.2 | 2.9 |
| | 3 | 1 | 0.1 | 0.6 | 1.0 | 2.5 |
| | | 2 | 0.2 | 0.2 | 1.0 | 2.0 |
| High TDS | 1 | 1 | 0.8 | 1.0 | 1.5 | 4.5 |
| | | 2 | 0.7 | 1.2 | 2.0 | 2.0 |
| | 2 | 1 | 1.0 | 1.2 | 2.0 | 3.0 |
| | | 2 | 1.0 | 1.2 | 1.5 | 4.0 |
| | 3 | 1 | 0.5 | 2.5 | 1.0 | 3.0 |
| | | 2 | 0.3 | 4.0 | 3.0 | 3.8 |
| Colored | 1 | 1 | 0.4 | 1.0 | 1.8 | 4.0 |
| | | 2 | 0.4 | 0.9 | 1.4 | 4.0 |
| | 2 | 1 | 0.4 | 0.4 | 1.8 | 3.7 |
| | | 2 | 0.5 | 0.8 | 1.7 | 3.9 |
| | 3 | 1 | 0.4 | 0.4 | 1.5 | 3.5 |
| | | 2 | 1.0 | 0.8 | 1.0 | 3.0 |
| Well | 1 | 1 | 0.3 | 0.5 | 2.3 | 4.0 |
| | | 2 | 0.4 | 0.5 | 1.5 | 3.5 |
| | 2 | 1 | 0.3 | 0.4 | 1.8 | 3.2 |
| | | 2 | 0.3 | 0.8 | 1.5 | 3.3 |
| | 3 | 1 | 0.1 | 0.5 | 2.0 | 3.0 |
| | | 2 | 0.3 | 0.3 | 1.0 | 2.0 |
| Organically Polluted | 1 | 1 | 0.3 | 0.8 | 2.0 | 4.1 |
| | | 2 | 0.3 | 0.7 | 1.5 | 3.3 |
| | 2 | 1 | 0.3 | 1.2 | 1.5 | 3.5 |
| | | 2 | 0.1 | 0.5 | 1.5 | 3.5 |
| | 3 | 1 | 0.2 | 0.2 | 1.0 | 3.0 |
| | | 2 | 0 | 0.5 | 1.5 | 1.0 |

## TABLE 28. Copper - Blank Tests (ppm)

(All samples contained deionized water)

| Operator 1 | Operator 2 | Operator 3 |
|---|---|---|
| Blank | Blank | Blank |
| Blank | Blank | Blank |
| Blank | Blank | 0.1 |
| Blank | Blank | Blank |
| 0.1 | Blank | Blank |
| Blank | Blank | 0.1 |
| Blank | Blank | Blank |
| 0.2 | Blank | 0.1 |
| Blank | Blank | 0.3 |
| Blank | Blank | Blank |
| 0.1 | Blank | 0.1 |
| 0.1 | Blank | 0.3 |
| Blank | Blank | Blank |
| Blank | Blank | Blank |
| 0.1 | Blank | Blank |

Figure 3. Copper Rings

## TABLE 29. Analysis of Qualifications Tests - Copper Ion
(Refer to Section 4.4 for explanation of terms)

### Analysis of Variance - All Ion Concentrations

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 1.778 | 2 | 0.889 | 3.372* |
| Ion Level | 0.495 | 3 | 0.165 | 0.247 |
| Water Samp | 8.737 | 4 | 2.184 | 3.790 |
| OPXIONLEV | 4.011 | 6 | 0.668 | 2.535* |
| OPXWATSAM | 4.610 | 8 | 0.576 | 2.186* |
| WATSMXIONL | 5.449 | 12 | 0.454 | 1.722 |
| Precision | 15.820 | 60 | 0.264 | |

$S_p^2 = 0.264$

$S_o^2 = 0.0156$

Third order interaction MS = 0.0637

### Average Errors of Measurement
(Measured Ion Concentration Minus Actual Ion Concentration)

| | Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| **Operator** | 0.4 | 0.7 | 1.5 | 3.0 |
| 1 | 0.03 | 0.10 | 0.19 | 0.54 |
| 2 | 0.07 | 0.07 | 0.07 | 0.31 |
| 3 | -0.09 | 0.30 | -0.10 | -0.41 |
| **Water Sample** | | | | |
| Turbid | -0.10 | -0.13 | -0.28 | -0.42 |
| High TDS | 0.32 | 1.15 | 0.33 | 0.38 |
| Colored | 0.12 | 0.02 | 0.03 | 0.68 |
| Wall | -0.12 | -0.20 | 0.18 | 0.17 |
| Organically Polluted | -0.20 | -0.05 | 0 | 0.08 |

| **Water Sample** | Operator | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Turbid | -0.03 | -0.23 | -0.45 |
| High TDS | 0.31 | 0.46 | 0.86 |
| Colored | 0.34 | 0.25 | 0.05 |
| Well | 0.22 | 0.05 | 0.25 |
| Organically Polluted | 0.22 | 0.11 | -0.59 |

TABLE 29. (Continued)

## Analysis of Variance for Each Ion Concentration

The ion concentration is 0.4 ppm

| Source | SS | DF | MS | F | |
|---|---|---|---|---|---|
| | | | | | $S_p^2 = 0.022$ |
| Operator | 0.139 | 2 | 0.069 | 3.200 | |
| Water Sample | 1.065 | 4 | 0.266 | 4.616* | $S_o^2 = 0^{(1)}$ |
| OPXWATSAM | 0.461 | 8 | 0.058 | 2.662* | $\underline{\overline{X}} = 0.403$ |
| Precision | 0.325 | 15 | 0.222 | | |

The ion concentration is 0.7 ppm

| Source | S | DF | MS | F | |
|---|---|---|---|---|---|
| | | | | | $S_p^2 = 0.122$ |
| Operator | 0.313 | 2 | 0.156 | 1.285 | |
| Water Sample | 7.562 | 4 | 1.890 | 2.458 | $S_o^2 = 0^{(1)}$ |
| OPXWATSAM | 6.154 | 8 | 0.769 | 6.323** | $\underline{\overline{X}} = 0.857$ |
| Precision | 1.825 | 15 | 0.122 | | |

The ion concentration is 1.5 ppm

| Source | S | DF | MS | F | |
|---|---|---|---|---|---|
| | | | | | $S_p^2 = 0.265$ |
| Operator | 0.425 | 2 | 0.212 | 0.800 | |
| Water Sample | 1.271 | 4 | 0.318 | 4.720* | $S_2^o = 0^{(1)}$ |
| OPXWATSAM | 0.539 | 8 | 0.067 | 0.254 | $\underline{\overline{X}} = 1.553$ |
| Precision | 3.980 | 15 | 0.265 | | |

The ion concentration is 3.0 ppm

| Source | S | DF | MS | F | |
|---|---|---|---|---|---|
| | | | | | $S_p^2 = 0.646$ |
| Operator | 4.913 | 2 | 2.456 | 3.802* | |
| Water Sample | 4.288 | 4 | 1.072 | 2.406 | $S_o^2 = 0.181$ |
| OPXWATSAM | 3.564 | 8 | 0.445 | 0.690 | $\underline{\overline{X}} = 3.147$ |
| Precision | 9.690 | 15 | 0.646 | | |

(1) If the F value for operator effect is not significant, we take $S_o^2 = 0$.

Table 29. (Continued)

Average Errors Obtained

| Operator | Average Error |
|---|---|
| 1 | 0.215 |
| 2 | 0.130 |
| 3 | -0.075 |
| **Water Sample** | |
| Turbid | -0.233 |
| High TDS | 0.546 |
| Colored | 0.212 |
| Well | 0.008 |
| Organically Polluted | -0.083 |
| **Ion Concentration** | |
| 0.4 ppm | 0.003 |
| 0.7 ppm | 0.157 |
| 1.5 ppm | 0.053 |
| 3.0 ppm | 0.147 |

encountered with the turbid water samples, which had also occurred during ruggedness testing in the second year's contract effort during work with turbid waters. This was apparently due to absorption of copper by the turbid matter. The data in Table 28 (p. 63) for the blank tests show no false positives greater than the lowest water test concentration of 0.4 ppm. A false positive (not significant, however) was obtained in 24% of the tests.

Referring to the method suggested in Section 4.4.4 (p. 38) for using the ring oven as a screening procedure, we see that it would appear to work quite well for this case. The distribution of results for each ion concentration for the 15 pairs of measurements are given in Table 30. Note again that these are rather tentative conclusions, as discussed in Section 4.4.4.

Figure 5 gives a bar graph illustrating the copper tests' efficacy for general screening. As can be seen from this figure, at the two levels above the 1.0 ppm decision concentration, a correct "go-no go" decision was made 100% of the time.

### Conclusions

The dithiooxamide-ring oven test for the copper ion appears to offer much promise for determination of copper in water. The average error does not exceed 0.16 ppm at any of the four ion levels tested. The precision is quite satisfactory, and little variability is shown for different operators. Effects were shown from the interaction of color-reagent temperature, and by ion concentration.

As a general scan method, the ring oven procedure shows great promise. At the levels above the 1 ppm decision concentration, the concenration is found to be equal to or greater than the decision level 30 out of 30 times.

### 5.1.2 Zinc

The zinc test was based upon the color formed by the reaction of $Zn^{+2}$ with 1-(2-pyridylazo)-2-naphthol (PAN). The original range for which this reagent was evaluated was from 1 to 20 ppm, with standard values of 1, 5, 10, and 20 ppm zinc.

TABLE 30. Distribution of Replicate Results Around Decision Level for Copper Qualifications Tests

Decision Concentration = 1 ppm

| Ring Oven Results | Sample Ion Concentration (ppm) 0.4 | 0.7 | 1.5 | 3.0 |
|---|---|---|---|---|
| Both Values ≥ 1 ppm(1) | 1 | 3 | 15 | 15 |
| Both Values < 1 ppm(2) | 13 | 10 | 0 | 0 |
| Other(3) | 1 | 2 | 0 | 0 |

(1) The ion concentration is deemed unacceptable

(2) The ion concentration is deemed acceptable.

(3) More Measurement is required before a decision can be made.

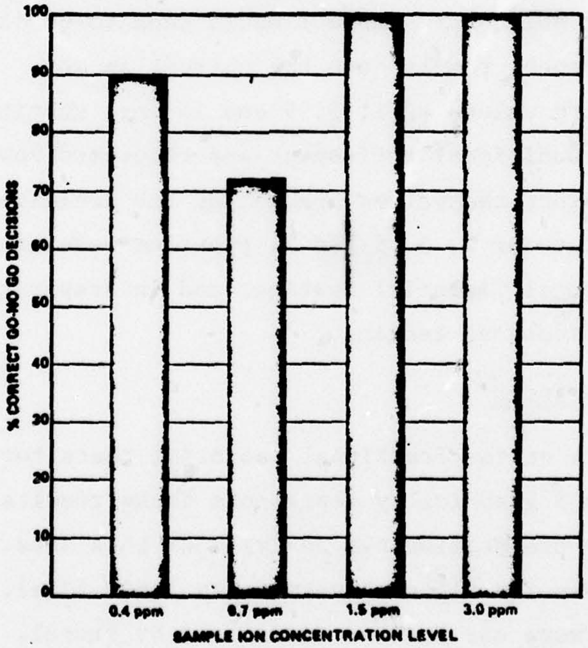


Figure 4. Percent Correct "Go-No Go" Decisions for Copper Ion (Based upon a decision concentration of 1 ppm)

## Procedure Adjustment

During preliminary work, when operator technique was being developed, it was decided to cut the amount of thioacetamide added to 2 µl. This limits the amount of $(NH_4)_2S$ deposited, making it easier for relatively inexperienced operators to form symmetrical rings. The procedure used to obtain all of the following results is given in Appendix C.

The metals cadmium, lead, copper, mercury, and iron also reacted with the pyridylazo-naphthol. These interferences were eliminated through precipitation as sulfides by thioacetamide (lead, cadmium, copper and mercury), or by precipitation as the hydroxides by ammonium hydroxide (iron). Further discussion of the interferences in the zinc test can be found in Reference (1).

## Operator Variability Tests

Initial standards used were 1, 5, 9, and 15 ppm zinc. The results of the sample analysis are shown in Table 31. The first erroneous result obtained by Operator No. 6 for sample T would seem to be due to failure to apply sample, as a repeat result gave the correct answer.

The standard values of 1, 5, 9 and 15 were submitted to the Army for approval. Some additional refinement was requested however, in order to bring closer together the values bracketing the decision level of 5 ppm. Accordingly, the values of 2, 5, 8 and 11 ppm zinc were used as standard values in the fractional factorial testing, and in preparation of permanent standards for qualifications testing.

## Fractional Factorial Tests

The results of the fractional factorial tests for zinc are given in Table 32. Figure 5 graphically represents these results. Tables 33(a), 33(b) and 33(c) give the statistical analysis of this data. As can be seen from the analysis for all observations in Table 33(a), several highly significant effects were encountered (indicated by stars). Detection reagent temperature, detection reagent age, and ion concentration all produced highly significant effects, as did interactions between color and reagent age, reagent temperature and ion concentration, and reagent age and ion

## TABLE 31. Operator Variability Tests - Zinc, Run No. 1

| **Sample** | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 5 (ppm) |
|---|---|---|---|
| A | 15.0 | >15.0 | >15.0 |
| B | Blank | 0.9 | < 1.0 |
| C | 9.0 | 6.0(7)* | 6.0(9) |
| D | 5.0 | 5.0 | 4.0 |
| E | 5.0 | 4.0 | 5.0 |
| F | 15.0 | >15.0 | >15.0 |
| G | 1.0 | 1.0 | 1.0 |
| H | 9.0 | 7.0(9) | >15.0 |
| I | 1.0 | 0.9 | 1.0 |
| J | 9.0 | 7.0 | 9.0 |
| K | 5.0 | 5.0 | 9.0 |
| L | 15.0 | >15.0 | >15.0 |
| M | 1.0 | 1.0 | 3.0 |
| N | 9.0 | 14.0(15) | 15.0(9) |
| O | 9.0 | 15.0 | 15.0(8) |
| P | 15.0 | >15.0 | >15.0 |
| Q | 5.0 | 6.0(5) | 3.0(4) |
| R | 15.0 | >15.0 | >15.0 |
| S | 1.0 | 1.0 | 1.0 |
| T | 5.0 | 5.0 | <1.0(5) |

15μl Samples

Standards: 1-5-9-15

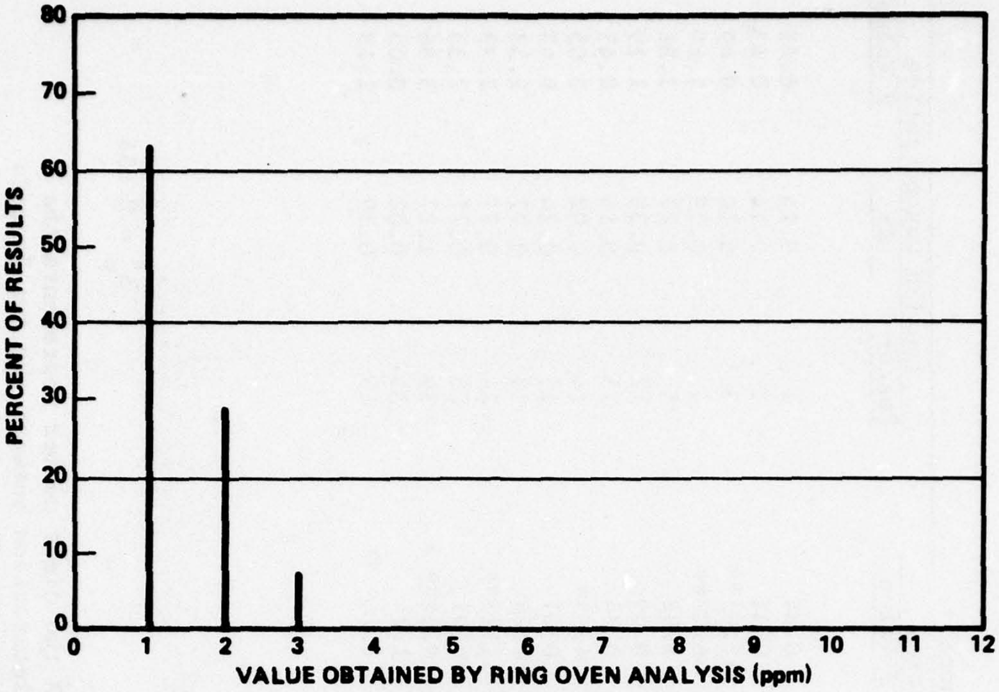
Decision Level: 5 ppm

*Number in parenthesis represents repeat analysis.

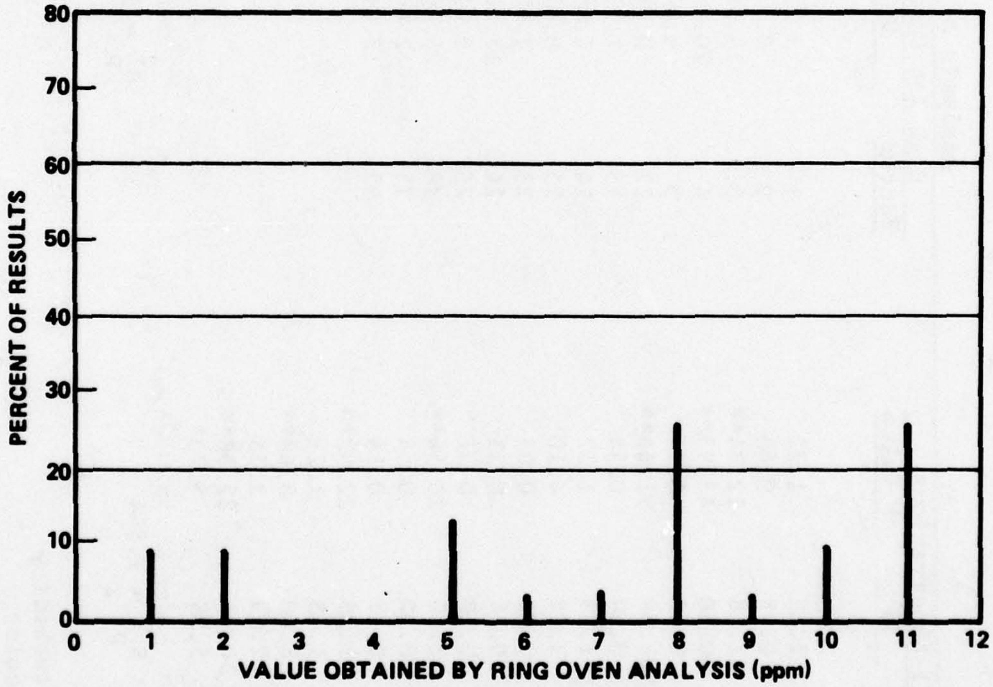
TABLE 32. Results of Zinc Fraction Factorial Tests (Refer to Table 11, p. 26 for actual sample content)

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 1 | 2 | 2 |
| b | 1 | 2 | 2 |
| c | 1 | <2 | <2 |
| d | 1 | <2 | <2 |
| e | 1 | <2 | <2 |
| f | 10 | 5 | 7 |
| g | 1 | <2 | 3 |
| g | 1 | <2 | 2 |
| i | 10 | 8 | 8 |
| j | 10 | 8 | 9 |
| k | 1 | <2 | <2 |
| l | 10 | 10 | 11 |
| m | 10 | 5 | 11 |
| n | 1 | <2 | 3 |
| o | 1 | <2 | <2 |
| p | 10 | <2 | 2 |
| q | 1 | <2 | 2 |
| r | 10 | 10 | 10 |
| s | 10 | 6 | 11 |
| t | 10 | <2 | 2 |
| u | 1 | 2 | 5 |
| v | 1 | <2 | 2 |
| w | 10 | <2 | 2 |
| x | 1 | <2 | <2 |
| y | 10 | 8 | 8 |
| z | 1 | <2 | <2 |
| aa | 10 | 5 | 8 |
| bb | 1 | <2 | 2 |
| cc | 10 | 8 | 11 |
| dd | 10 | 11 | 11 |
| ee | 10 | 5 | 8 |
| ff | 10 | 11 | 11 |

Standards: 2 - 5 - 8 -11
Operator No. 4



ACTUAL VALUE 1ppm ZINC



ACTUAL VALUE 10ppm ZINC

Figure 5. Percent Distribution of Zinc Fractional Factorial Test Results at Tested Ion Concentrations

TABLE 33(a). Statistical Analysis of Zinc Fractional Factorial Tests

$S_p^2/2$ used for residual mean square

| Analysis of Variance | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| All Observations | | | High Ion Concentration | | | Low Ion Concentration | | |
| **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** |
| 1 | 1.13 | 1.22 | 1 | 1.27 | 0.84 | 1 | 0.14 | 0.43 |
| 2 | 0.78 | 0.85 | 2 | 0.77 | 0.41 | 2 | 0.14 | 0.43 |
| 3 | 11.28 | 12.24** | 3 | 19.14 | 12.63** | 3 | 0.14 | 0.43 |
| 4 | 40.50 | 43.93** | 4 | 70.14 | 46.28** | 4 | 0.39 | 1.19 |
| 5 | 0.50 | 0.54 | 5 | 4.52 | 2.98 | 5 | 1.27 | 3.86 |
| 6 | 84.50 | 91.66** | 12 | 0.14 | 0.09 | 12 | 0.39 | 1.19 |
| 12 | 0.50 | 0.54 | 13 | 1.27 | 0.84 | 13 | 0.14 | 0.43 |
| 13 | 1.13 | 1.22 | 14 | 6.89 | 4.55* | 14 | 0.02 | 0.05 |
| 14 | 3.78 | 4.10 | 15 | 0.02 | 0.01 | 15 | 0.14 | 0.43 |
| 15 | 0.03 | 0.03 | 23 | 2.64 | 1.74 | 23 | 0.77 | 2.33 |
| 16 | 0.28 | 0.31 | 24 | 17.02 | 11.23** | 24 | 0.77 | 2.33 |
| 23 | 0.28 | 0.31 | 25 | 0.02 | 0.01 | 25 | 0.77 | 2.33 |
| 24 | 12.50 | 13.56** | 34 | 28.89 | 19.06** | 34 | 1.27 | 3.86 |
| 25 | 0.50 | 0.54 | 35 | 2.64 | 1.74 | 35 | 0.02 | 0.05 |
| 26 | 0.13 | 0.14 | 45 | 2.64 | 1.74 | 45 | 0.39 | 1.19 |
| 34 | 21.13 | 22.92** | | | | | | |
| 35 | 1.13 | 1.22 | | | | | | |
| 36 | 8.00 | 8.68** | | | | | | |
| 45 | 2.53 | 2.75 | | | | | | |
| 46 | 30.03 | 32.58** | | | | | | |
| 56 | 5.28 | 5.73* | | | | | | |
| $S_p^2 = 1.844$ | | | $S_p^2 = 3.013$ | | | $S_p^2 = 0.656$ | | |

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 33(b). Statistical Analysis of Zinc Fractional Factorial Tests

### Analysis of Variance - All Observations

Residual Mean Square = 2.331†

| Factor | SS | F Value |
|---|---|---|
| 1 | 1.13 | 0.48 |
| 2 | 0.78 | 0.34 |
| 3 | 11.28 | 4.84 |
| 4 | 40.50 | 17.37** |
| 5 | 0.50 | 0.21 |
| 6 | 84.50 | 36.25** |
| 12 | 0.50 | 0.21 |
| 13 | 1.13 | 0.48 |
| 14 | 3.78 | 1.62 |
| 15 | 0.03 | 0.01 |
| 16 | 0.28 | 0.12 |
| 23 | 0.28 | 0.12 |
| 24 | 12.50 | 5.36* |
| 25 | 0.50 | 0.21 |
| 26 | 0.13 | 0.05 |
| 34 | 21.13 | 9.06* |
| 35 | 1.13 | 0.48 |
| 36 | 8.00 | 3.43 |
| 45 | 2.53 | 1.09 |
| 46 | 30.03 | 12.88** |
| 56 | 5.28 | 2.27 |

†For this table, the lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

TABLE 33(c). Statistical Analysis of Zinc Fractional Factorial Tests

The Average Errors for the High and Low Levels of Each Factor Are:

|  | (All observations) |  |  | (At the high ion concentration) |  |  | (At the low ion concentration) |  |
|---|---|---|---|---|---|---|---|---|
|  | High | Low |  | High | Low |  | High | Low |
| 1 | -1.281 | -0.906 | 1 | -3.000 | -2.438 | 1 | 0.438 | 0.625 |
| 2 | -1.250 | -0.938 | 2 | -2.938 | -2.500 | 2 | 0.438 | 0.625 |
| 3 | -1.688 | -0.500 | 3 | -3.813 | -1.625 | 3 | 0.438 | 0.625 |
| 4 | 0.031 | -2.219 | 4 | -0.625 | -4.813 | 4 | 0.688 | 0.375 |
| 5 | -0.969 | -1.219 | 5 | -2.188 | -3.250 | 5 | 0.250 | 0.813 |
| 6 | -2.719 | 0.531 |  |  |  |  |  |  |

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

concentration. The 5 ppm value found for sample u (nominal value equal to 1 ppm Zn) may be due to detection reagent temperature and age, while the low values obtained for samples p and t may be due to elevated reagent temperature. Most of these effects were confirmed, although to a lesser degree, by the alternate statistical analysis for all observations in Table 33(b). Table 34 summarizes the factors' effects for all observations.

In addition, as with copper, all of the effects discussed in the preceding paragraph are much more significant at high ion concentration than at the low ion concentration. The values at the low ion concentration also showed a smaller standard deviation, resulting in a greater precision, and a smaller average error than was demonstrated at the high concentration.

## Qualifications Testing

The results of the qualifications testing for the zinc ion are presented in Table 35, while Table 36 shows the results of the blank tests. Table 37 gives the statistical analysis of these results.

For this ion, the standards were 2, 5, 8, and 11 ppm and the ion concentrations used were 1, 3, 7 and 10 ppm. Figure 6 shows the permanent standards used in qualifications testing. A number of measurements were recorded as <2 (below the lowest standard). In the analysis, these measurements were taken to be 1 ppm. A number of measurements were recorded as >11. These measurements were arbitrarily assigned the value of 12 ppm. Most of the data seems reasonably consistent, although Operator 1 recorded 10 and 2 for the colored water at 3 ppm ion concentration, and Operator 2 recorded lower measurements at 10 ppm than at 7 ppm. (This may be due to overapplication of reagent.) The few cases where large discrepancies occurred between the two measurements should probably not happen in field use of the equipment since a conscientious operator, upon seeing the large variation, should make additional measurements to resolve the discrepancies.

For the analysis using all the ion concentrations, we see that the variability among operators and the variability of measurements at the different ion concentrations give highly significant results. The variability

TABLE 34. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Zinc

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | - | - | - | - | - | - |
| Color | - | - | - | ** | - | - |
| Detection Reagent Temperature | - | - | ** | ** | - | ** |
| Reagent Age | - | ** | ** | ** | - | ** |
| Chlorine Concentration | - | - | - | - | - | * |
| Ion Concentration | - | - | ** | ** | * | ** |

- = no significant effect
* = significant effect
** = highly significant effect

## TABLE 35. Zinc Qualifications Tests

Standards: 2 - 5 - 8 - 11

| Water Sample | Operator | Measurement | Ion Concentration | | | |
|---|---|---|---|---|---|---|
| | | | 1 ppm | 3 ppm | 7 ppm | 10 ppm |
| Turbid | 1 | 1 | 2 | 5 | 7 | 7 |
| | | 2 | <2 | 7 | >11 | 10 |
| | 2 | 1 | <2 | 2 | 4 | 8 |
| | | 2 | 0 | 2 | 7 | 8 |
| | 3 | 1 | 2 | 4 | 8 | 7 |
| | | 2 | 2 | 3 | 8 | 10 |
| High TDS | 1 | 1 | <2 | 5 | 7 | >11 |
| | | 2 | <2 | 8 | 7 | 11 |
| | 2 | 1 | 2 | 2 | 6 | 6 |
| | | 2 | <2 | 5 | 7 | 11 |
| | 3 | 1 | <2 | 5 | 10 | 10 |
| | | 2 | 2 | 8 | 9 | 10 |
| Colored | 1 | 1 | 2 | 10 | 7 | 7 |
| | | 2 | <2 | 2 | 8 | 10 |
| | 2 | 1 | <2 | 3 | 8 | 6 |
| | | 2 | 2 | 2 | 9 | 6 |
| | 3 | 1 | 1 | 4 | 4 | 11 |
| | | 2 | 2 | 2 | 5 | 11 |
| Well | 1 | 1 | 2 | 4 | >11 | 11 |
| | | 2 | 3 | 2 | 5 | 9 |
| | 2 | 1 | <2 | 4 | 2 | 5 |
| | | 2 | 2 | 4 | 8 | 7 |
| | 3 | 1 | <2 | 5 | 7 | 10 |
| | | 2 | <2 | 5 | 5 | 8 |
| Organically Polluted | 1 | 1 | 3 | 5 | 3 | 6 |
| | | 2 | 3 | <2 | 5 | 11 |
| | 2 | 1 | <2 | 4 | 8 | 8 |
| | | 2 | <2 | <2 | 6 | 8 |
| | 3 | 1 | 3 | 3 | 6 | 8 |
| | | 2 | <2 | 4 | 8 | 11 |

TABLE 36. Zinc - Blank Tests (ppm)
(All samples consisted of deionized water)

| Operator 1 | Operator 2 | Operator 3 |
|---|---|---|
| 2 | Blank | Blank |
| 2 | Blank | <2 |
| 2 | Blank | <2 |
| <2 | Blank | <2 |
| 2 | Blank | 2 |
| <2 | Blank | <2 |
| 2 | Blank | <2 |
| 2 | Blank | Blank |
| 3 | Blank | <2 |
| 2 | Blank | <1 |
| <2 | 2 | <2 |
| <2 | Blank | <1 |
| 2 | <2 | <1 |
| 2 | Blank | Blank |
| 5 | Blank | Blank |

## TABLE 37 - Analysis of Qualifications Tests - Zinc Ion
(Refer to Section 4.4 for explanation of terms)

Analysis of Variance - All Ion Concentrations

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 46.867 | 2 | 23.433 | 7.266** |
| Ion Level | 88.825 | 3 | 29.608 | 12.689** |
| Water Sample | 19.450 | 4 | 4.862 | 2.424 |
| OPXIONLEV | 14.000 | 6 | 2.333 | 0.724 |
| OPXWATSAM | 16.050 | 8 | 2.006 | 0.622 |
| WATSMXIONL | 29.217 | 12 | 2.435 | 0.755 |
| Precision | 193.500 | 60 | 3.225 | |

$S_p^2 = 3.225$

$S_o^2 = 0.505$

Third Order Interaction

MS = 4.503

Average Errors of Measurements
(Measured Ion Concentration Minus Actual Ion Concentration)

| | Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| Operator | 1 | 3 | 7 | 10 |
| 1 | 1.10 | 1.90 | 0.30 | -0.60 |
| 2 | 0.20 | -0.10 | -0.50 | -2.70 |
| 3 | 0.60 | 1.30 | 0.00 | -0.40 |
| Water Sample | | | | |
| Turbid | 0.33 | 0.83 | 0.67 | -1.67 |
| High TDS | 0.33 | 2.50 | 0.67 | 0.00 |
| Colored | 0.50 | 0.83 | -0.17 | -1.50 |
| Well | 0.67 | 1.00 | -0.50 | -1.67 |
| Organically Polluted | 1.33 | 0.00 | -1.00 | -1.33 |

| | Operator | | |
|---|---|---|---|
| Water Sample | 1 | 2 | 3 |
| Turbid | 1.13 | -1.25 | 0.25 |
| High TDS | 1.25 | -0.25 | 1.63 |
| Colored | 0.63 | -0.63 | -0.25 |
| Well | 0.75 | -1.13 | 0.00 |
| Organically Polluted | -0.38 | -0.63 | 0.25 |

## TABLE 37. (Continued)

### Analysis of Variance for Each Ion Concentration

The ion concentration is 1 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 4.067 | 2 | 2.033 | 3.588 |
| Water Sample | 4.133 | 4 | 1.033 | 0.805 |
| OPXWATSAM | 10.267 | 8 | 1.283 | 2.265 |
| Precision | 8.500 | 15 | 0.567 | |

$S_p^2 = 0.567$

$(S_o^2 = 0.147)^{(1)}$

$\bar{X} = 1.633$

The ion concentration is 3 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 21.067 | 2 | 10.533 | 2.412 |
| Water Sample | 19.800 | 4 | 4.950 | 1.489 |
| OPXWATSAM | 26.600 | 8 | 3.325 | 0.761 |
| Precision | 65.500 | 15 | 4.367 | |

$S_p^2 = 4.367$

$(S_o^2 = 0.617)^{(1)}$

$\bar{X} = 4.033$

The ion concentration is 7 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 3.267 | 2 | 1.633 | 0.350 |
| Water Sample | 12.867 | 4 | 3.217 | 0.391 |
| OPWATSAM | 65.733 | 8 | 8.217 | 1.761 |
| Precision | 70.000 | 15 | 4.667 | |

$S_p^2 = 4.667$

$(S_o^2 = -0.303)^{(1)}$

$\bar{X} = 6.933$

The ion concentration is 10 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 32.467 | 2 | 16.233 | 4.919* |
| Water Sample | 11.867 | 4 | 2.967 | 1.102 |
| OPXWATSAM | 21.533 | 8 | 2.692 | 0.816 |
| Precision | 49.500 | 15 | 3.300 | |

$S_p^2 = 3.300$

$S_o^2 = 1.293$

$\bar{X} = 9.767$

---

(1) If the F value for operator effect is not significant $S_o^2$ should be considered to be zero.

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EVALUATION OF THE RING OVEN TECHNIQUE FOR WATER MONITORING.(U)
OCT 77    R E SNYDER, M E TONKIN, A M MCKISSICK    DAMD17-76-C-6049

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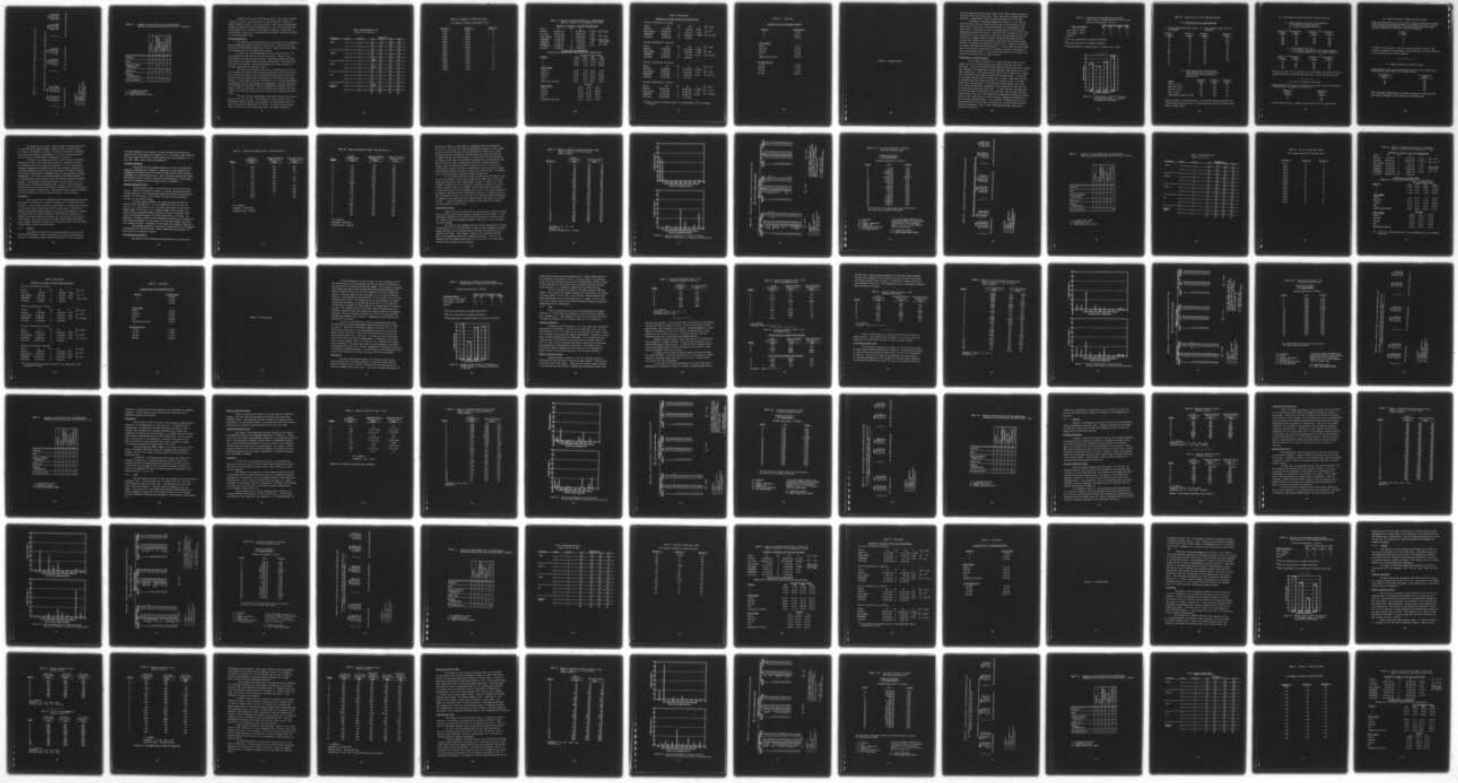


TABLE 37. (Continued)

Average Errors by Individual Factors

| Operator | Average Error |
|---|---|
| 1 | 0.675 |
| 2 | -0.775 |
| 3 | 0.375 |
| **Water Sample** | |
| Turbid | 0.042 |
| High TDS | 0.875 |
| Colored | -0.083 |
| Well | -0.125 |
| Organically Polluted | -0.250 |
| **Ion Concentration** | |
| 1 ppm | 0.633 |
| 3 ppm | 1.033 |
| 7 ppm | -0.067 |
| 10 ppm | -0.233 |

Figure 6. Zinc Rings

due to different water samples is not significant, and none of the interactions are significant. The magnitude of the operator effect (measured by $S_o^2$) is considerably less than the variability of repeated measurements by the same operator measured by $S_p^2$). The values of $S_p^2$ at the high (10 ppm) and low (1 ppm) ion concentrations are very close to those obtained at the same concentrations in the fractional factorial tests. The average errors for the individual ion concentrations do not appear excessive, the maximum positive error occurring at the 3 ppm zinc level being 1.0 ppm. For the individual water samples, the greatest positive error was obtained with the high TDS sample, as in the case of copper. This error, however, amounted to a value of less than 1 ppm, which is very good for even an atomic absorption procedure in this range. Only one significant false positive was obtained in the blank testing, this at the decision concentration of 5 ppm. This occurred in only 2% of the cases.

At each ion level, fifteen pairs of measurements were made for a total of 60 pairs of measurements. Table 38 shows the distribution of these measurements around the decision concentration. Referring to the method suggested in Section 4.4.4 (p. 38) for use of the ring oven procedure as a screening test, we see that it would appear to work very well for this case. When the ion concentration is close to 5 ppm, we would frequently need to make additional measurements. When the ion level was far from 5 ppm, we would determine this from the initial measurements. Figure 7 illustrates this analysis for general screening purposes graphically. As can be seen in this graph, at the level of 10 ppm zinc, 100% of the number of the "go-no go" decisions were made correctly, while at the level slightly above the 5 ppm decision level, 87% of the "go-no go" decisions as to water potability were correct.

## Conclusions

The ring oven can be used as a screening tool for zinc in natural water with some success. Although greater error at higher ion concentrations than at lower concentrations is demonstrated, it can be seen from the discussion in the preceding section that at the maximum ion concentration tested (10 ppm Zn), the ring oven overwhelmingly places the level over the decision level of 5 ppm. At levels near to, but above, the decision level (e.g., 7 ppm)

TABLE 38. Distribution of Replicate Results Around Decision Level for Zinc Qualifications Tests

Decision Concentration - 5 ppm

| | Sample Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| Ring Oven Results | 1 | 3 | 5 | 7 |
| Both Values ≥ 5(1) | 0 | 4 | 11 | 15 |
| Both Values < 5(2) | 14 | 8 | 0 | 0 |
| Other(3) | 1 | 3 | 4 | 0 |

(1) The ion concentration is deemed unacceptable.

(2) The ion concentrations is deemed acceptable.

(3) More measurement is required before a decision can be made.

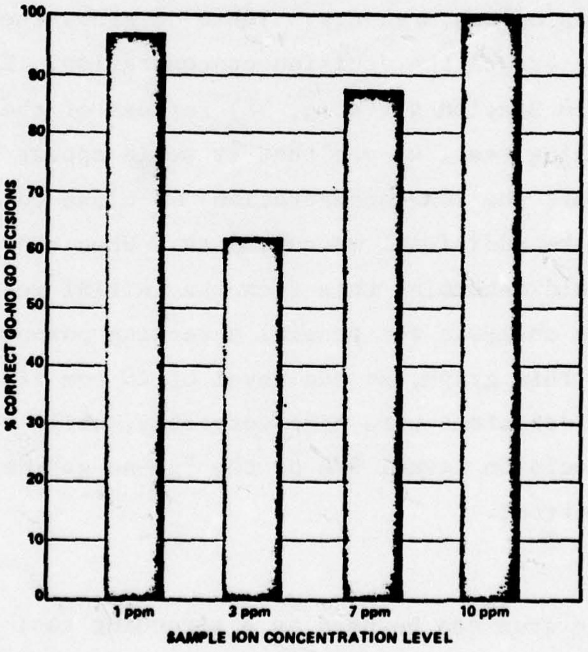


Figure 7. Percent Correct "Go-No Go" Decisions for Zinc (Based on a decision concentration of 5 ppm)

a majority of the samples are placed at levels above the decision concentration. This majority could show an increase in a field situation by making successive measurements on the same sample as discussed in Section 4.

One cause of low results in this test, such as those obtained on well water at the 7 ppm and 10 ppm level by Operator 2, is over-application of the reagent due to excessive spraying. This over-application, which tends to obscure ring intensity, should prove easily correctable through the use of meter sprays. These were investigated to a slight extent during this program; however, lack of time and funds prevented further pursuance of this item. Highly significant effects were shown for ion concentration, reagent age and temperature; and for the interactions between color-reagent age, reagent temperature-reagent age, ion concentration-reagent age and ion concentration-reagent temperature.

### 5.1.3 Magnesium

The reagent selected for magnesium, p-nitrophenylazo-resorcinol (Magneson) was originally evaluated over the concentration range of 10 to 5000 ppm magnesium. Standard values used to cover this range were 10, 100, 500, 1000, 2500 and 5000 ppm magnesium.

#### Procedure Adjustment

The separation procedure designed originally to eliminate iron, chromium, copper, and mercury interference was considered unnecessary, because if sufficient quantities of these metals are present to interfere with the magnesium test, the water is unusable in any case. For example, 60 ppm iron does not present an interference in the Mg test, and this is 200 times the iron decision level of 0.3 ppm. Similarly, high levels of the other metals are required before interference in the magnesium test occurs. In place of the separation procedure, then, an acid wash was used. This resulted in better-formed rings, aiding in quantitation. The procedure used for the statistical evaluation of the ring oven procedure for magnesium is given in Appendix C.

#### Operator Variabilty Tests

Using the standard values of 25, 125, 300, 500 and 1000 ppm magnesium, twenty synthetic water samples were analyzed by each operator. The results are presented in Table 39. Five standards were used because some difficulty had been encountered by the operators in differentiating between 300 and 500 ppm Mg during technique practice. As can be seen from the data in Table 38, this proved to be the case in the analysis of the samples.

For this reason, the 300 ppm Mg standard was dropped, and the 20 unknowns were again analyzed using the ring oven technique. The results are given in Table 40. Use of the four standard values of 25, 125, 500 and 1000 ppm Mg gave more satisfactory results. The data in Table 40 also suggested that we cannot differentiate between 300 and 500 ppm (i.e., Samples No. B and H).

The values of 25, 125, 500 and 1000 ppm Mg were then submitted to the Army for use as permanent standards. At the Army's request, Atlantic Research performed limited laboratory work to narrow the range, at the same time discarding the 125 ppm decision level in favor of the 150 ppm decision level. Thus, the approved standards used for fractional factorial testing, production of permanent standards, and qualifications testing were 50, 150, 300 and 500 ppm magnesium.

## Fractional Factorial Testing

The results of the magnesium fractional factorial tests are given in Table 41. The sample content of the factors tested in each sample can be obtained from Table 11 (p. 26). Figure 8 represents these results graphically.

Tables 42(a), 42(b) and 42(c) give the statistical analysis of these sample results. Table 42(a) shows that for the magnesium test, several single factors (reagent temperature, reagent age, and ion concentration) and one interaction (reagent age/ion concentration) show highly significant effects, indicated by a double star beside the respective F values. This is fairly well confirmed by the supplementary analysis performed for all observations as shown in Table 42(c). At the two individual ion concentrations (the high and the low level), similar effects are observed. Table 43 summarizes these effects for all observations.

TABLE 39. Operator Variability Tests - Magnesium, Run No. 1

| Sample | Actual Mg Concentration (ppm) | Mg found, Operator 1 (ppm) | Mg found, Operator 2 (ppm) |
|---|---|---|---|
| A | Blank | Blank | Blank |
| B | 300 | 125 | 500 |
| C | 25 | <25 | 125 |
| D | 500 | 125 | 1000 |
| E | 500 | 500 | 1000 |
| F | 125 | <25 | 125 |
| G | 1000 | 1000 | 1000 |
| H | 300 | 100 | 100 |
| I | 125 | 125 | 125 |
| J | 25 | 125 | <25 |
| K | 125 | <25 | 125 |
| L | 300 | 125 | 300 |
| M | 125 | 100 | 125 |
| N | 25 | <25 | 25 |
| O | 125 | 25 | 125 |
| P | 1000 | 1000 | 1000 |
| Q | 500 | 1000 | 500 |
| R | 125 | <25 | 25 |
| S | 25 | <25 | 125 |
| T | 300 | 25 | 500 |

Standards Used: 25-125-300-500-1000 ppm

Decision Levels: 125-150 ppm

15 µl Samples

## TABLE 40. Operator Variability Tests - Magnesium, Run No. 2

| Sample | Actual Mg Concentration (ppm) | Mg found, Operator 1 (ppm) | Mg found, Operator 2 (ppm) |
|---|---|---|---|
| A | Blank | Blank | <25 |
| B | 300 | 125 | 500 |
| C | 25 | 25 | 125 |
| D | 500 | 500 | 500 |
| E | 500 | 500 | 500 |
| F | 125 | 25 | 300 |
| G | 1000 | 1000 | 1000 |
| H | 300 | 125 | 500 |
| I | 125 | 125 | 125 |
| J | 25 | <25 | 25 |
| K | 125 | 125 | 125 |
| L | 300 | 300 | 500 |
| M | 125 | 125 | 300 |
| N | 25 | 25 | 125 |
| O | 125 | 25 | 125 |
| P | 1000 | 1000 | 1000 |
| Q | 500 | 300 | 500 |
| R | 125 | 125 | 125 |
| S | 25 | <25 | 50 |
| T | 300 | 300 | 500 |

Standards: 25 - 125 - 500 - 1000

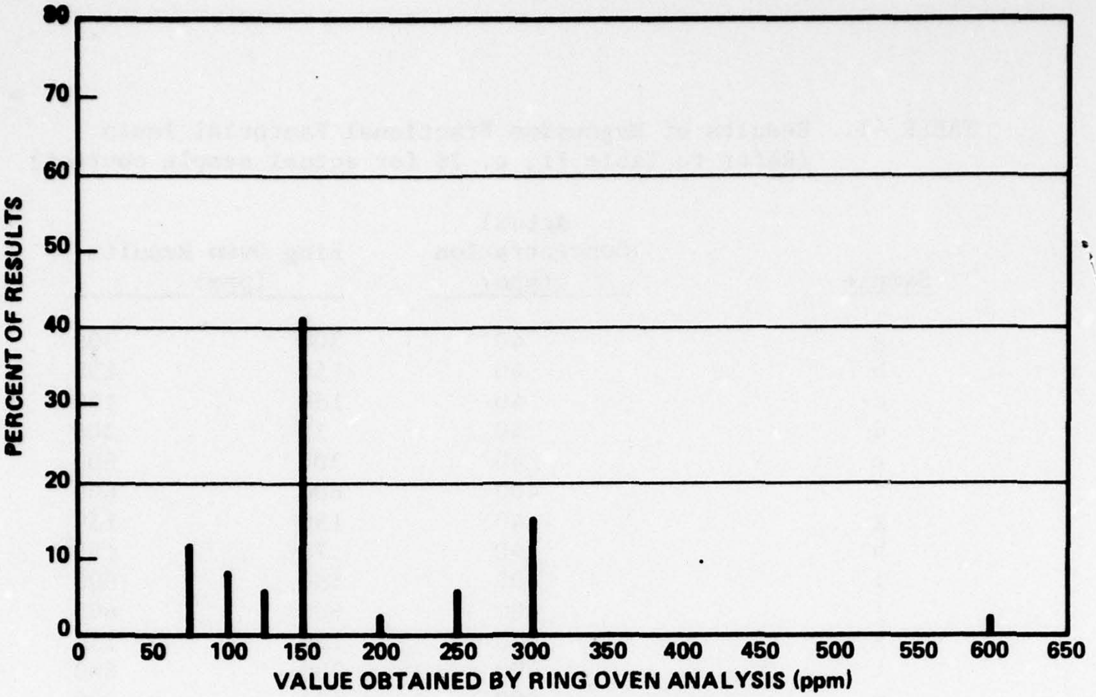
Decision Levels: 125-150 ppm

15 µl Samples

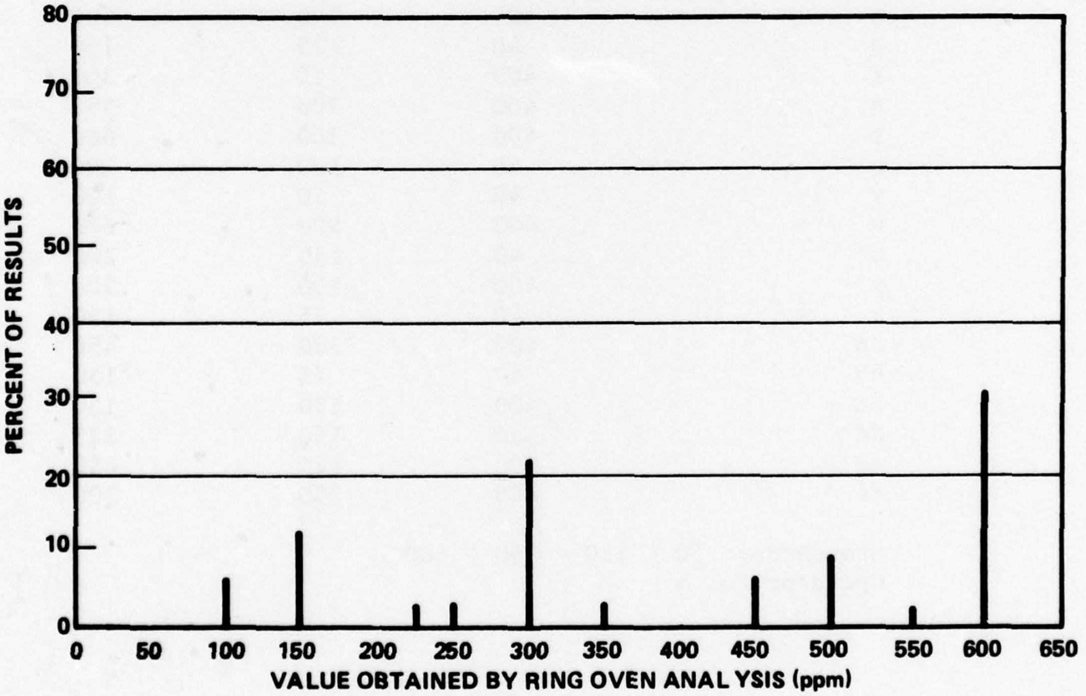
TABLE 41. Results of Magnesium Fractional Factorial Tests (Refer to Table 11, p. 26 for actual sample content)

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 40 | 300 | 300 |
| b | 40 | 150 | 150 |
| c | 40 | 150 | 150 |
| d | 40 | 75 | 300 |
| e | 40 | 300 | 600 |
| f | 400 | 600 | 600 |
| g | 40 | 150 | 150 |
| h | 40 | 75 | 150 |
| i | 400 | 550 | 600 |
| j | 400 | 600 | 600 |
| k | 40 | 150 | 250 |
| l | 400 | 300 | 600 |
| m | 400 | 500 | 600 |
| n | 40 | 150 | 300 |
| o | 40 | 250 | 300 |
| p | 400 | 500 | 600 |
| q | 40 | 125 | 150 |
| r | 400 | 150 | 300 |
| s | 400 | 300 | 350 |
| t | 400 | 300 | 600 |
| u | 40 | 100 | 100 |
| v | 40 | 50 | 100 |
| w | 400 | 500 | 600 |
| x | 40 | 150 | 200 |
| y | 400 | 100 | 300 |
| z | 40 | 75 | 150 |
| aa | 400 | 300 | 450 |
| bb | 40 | 75 | 150 |
| cc | 400 | 150 | 150 |
| dd | 400 | 150 | 225 |
| ee | 400 | 125 | 450 |
| ff | 400 | 250 | 300 |

Standards: 50 - 150 - 300 - 600
Operator No. 4



ACTUAL VALUE 40ppm MAGNESIUM



ACTUAL VALUE 400ppm MAGNESIUM

Figure 8. Percent Distribution of Magnesium Fractional Factorial Test Results at Tested Ion Concentrations

TABLE 42(a). Statistical Analysis of Magnesium Fractional Factorial Tests

**$S_p^2/2$ used for residual mean square**

**Analysis of Variance**

| All Observations | | | High Ion Concentration | | | Low Ion Concentration | | |
|---|---|---|---|---|---|---|---|---|
| **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** |
| 1 | 825.20 | 0.17 | 1 | 156.25 | 0.02 | 1 | 791.02 | 0.26 |
| 2 | 27,465.82 | 5.75* | 2 | 6,601.56 | 1.02 | 2 | 23,447.27 | 7.57* |
| 3 | 66,830.82 | 13.98** | 3 | 59,414.06 | 9.19** | 3 | 14,853.52 | 4.80* |
| 4 | 293,090.82 | 61.31** | 4 | 288,906.25 | 44.69** | 4 | 52,041.02 | 16.81** |
| 5 | 239.26 | 0.05 | 5 | 18,906.25 | 2.92 | 5 | 13,369.14 | 4.32 |
| 6 | 168,562.70 | 35.26** | 12 | 11,289.06 | 1.75 | 12 | 1,181.64 | 0.38 |
| 12 | 2,583.01 | 0.54 | 13 | 1,914.00 | 0.30 | 13 | 1,650.39 | 0.53 |
| 13 | 4.88 | 0.00 | 14 | 3,906.25 | 0.60 | 14 | 9.77 | 0.00 |
| 14 | 1,762.70 | 0.37 | 15 | 156.25 | 0.02 | 15 | 3,525.39 | 1.14 |
| 15 | 2,583.01 | 0.54 | 23 | 156.25 | 0.02 | 23 | 9,384.77 | 3.03 |
| 16 | 122.07 | 0.03 | 24 | 39.00 | 0.01 | 24 | 4,306.64 | 1.39 |
| 23 | 5,981.45 | 1.25 | 25 | 351.56 | 0.05 | 25 | 4,306.64 | 1.39 |
| 24 | 1,762.70 | 0.37 | 34 | 1,914.06 | 0.30 | 34 | 2,197.27 | 0.71 |
| 25 | 1,098.63 | 0.23 | 35 | 1,914.06 | 0.30 | 35 | 478.52 | 0.15 |
| 26 | 2,583.01 | 0.54 | 45 | 156.25 | 0.02 | 45 | 2,822.27 | 0.91 |
| 34 | 4.88 | 0.00 | | | | | | |
| 35 | 2,153.32 | 0.45 | | | | | | |
| 36 | 7,426.76 | 1.55 | | | | | | |
| 45 | 2,153.32 | 0.45 | | | | | | |
| 46 | 43,856.45 | 10.01** | | | | | | |
| 56 | 32,036.13 | 6.70* | | | | | | |
| $S_p^2 = 9,561$ | | | $S_p^2 = 12,930$ | | | $S_p^2 = 6,191$ | | |

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 42(b). Statistical Analysis of Magnesium Fractional Factorial Tests

### Analysis of Variance - All Observations

Residual Mean Square = 3,157.23†

| Factor | SS | F Value |
|---|---|---|
| 1 | 825.20 | 0.26 |
| 2 | 27,465.82 | 8.70* |
| 3 | 66,840.82 | 21.17** |
| 4 | 293,090.82 | 92.83** |
| 5 | 239.26 | 0.08 |
| 6 | 168,562.70 | 53.39** |
| 12 | 2,583.01 | 0.82 |
| 13 | 4.88 | 0.00 |
| 14 | 1,762.70 | 0.56 |
| 15 | 2,583.01 | 0.82 |
| 16 | 122.07 | 0.04 |
| 23 | 5,981.45 | 1.89 |
| 24 | 1,762.70 | 0.56 |
| 25 | 1,098.63 | 0.35 |
| 26 | 2,583.01 | 0.82 |
| 34 | 4.88 | 0.00 |
| 35 | 2,153.32 | 0.68 |
| 36 | 7,426.76 | 2.35 |
| 45 | 2,153.32 | 0.68 |
| 46 | 47,856.45 | 15.16** |
| 56 | 32,036.13 | 10.15** |

† For this table, the lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

TABLE 42(c). Statistical Analysis of Magnesium Fractional Factorial Tests

The Average Errors for the High and Low Levels of Each Factor Are:

| | High | Low |
|---|---|---|
| 1 | 64.375 | 74.531 |
| 2 | 40.156 | 98.740 |
| 3 | 23.750 | 115.156 |
| 4 | -26.250 | 165.156 |
| 5 | 66.719 | 72.188 |
| 6 | -3.125 | 142.031 |

(For all observations)

| | High | Low |
|---|---|---|
| 1 | -6.250 | 0.00 |
| 2 | -23.438 | 17.188 |
| 3 | -64.063 | 57.813 |
| 4 | -137.500 | 131.250 |
| 5 | -37.500 | 31.250 |

(For high ion concentration)

| | High | Low |
|---|---|---|
| 1 | 135.00 | 149.063 |
| 2 | 103.750 | 180.313 |
| 3 | 111.563 | 172.500 |
| 4 | 85.000 | 199.063 |
| 5 | 170.938 | 113.125 |

(For low ion concentration)

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

TABLE 43. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Magnesium

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | - | - | - | - | - | - |
| Color | - | * | - | - | - | - |
| Detection Reagent Temperature | - | - | ** | - | - | - |
| Reagent Age | - | - | - | ** | - | ** |
| Chlorine Concentration | - | - | - | - | - | * |
| Ion Concentration | - | - | - | ** | * | ** |

- = no significant effect
* = significant effect
** = highly significant effect

Looking at the actual fractional factorial test results as shown in Table 41 (p. 91), one observes that at the 40 ppm level, results are almost uniformly too high. This also proved to occur in the qualifications testing, as discussed in the following section. The reason for these high results appears to be inherent in the samples themselves, rather than in the procedure. This factor is discussed in more detail following the results of the qualifications tests.

## Qualifications Tests

The results of the qualifications and blank tests for the magnesium ion are presented in Tables 44 and 45, respectively. Table 46 gives the results of the statistical analysis of the data. Figure 9 shows the permanent standards used in the qualifications testing.

For this ion, the standards were 50, 150, 300 and 600 ppm. The ion concentrations used were 40, 100, 200 and 400 ppm. Several of the observations at 40 ppm were much too high. Repeat measurements were made at 40 ppm and the values obtained were quite reasonable. The original data was used in the analysis. Also the measurements at 400 ppm tended to be too high, especially for Operators 2 and 3.

The analysis of variance table shows a significant effect due to the different ion concentrations and highly significant effects due to operator variability and also for the operator/concentration level interaction. From the table of average errors for operator at the different ion concentrations, it would appear that this is primarily due to the high measurements by Operators 2 and 3 at the 400 ppm ion concentration. This may be because of the tendency of the rings to blur as concentration increases, which is largely a matter of technique. This is supported by the highly significant effects due to operator variability and to operator/ion concentration interaction.

The value for $S_p^2$ is considerably below that found in the fractional factorial tests for this ion. The estimate for operator effect, $S_o^2$, is considerably smaller than $S_p^2$. As was expected, a large positive error was found at the low ion concentration of 40 ppm. It is felt that this error is not real, but is due to some action within the samples themselves.

**TABLE 44. Magnesium Qualifications Tests**

**Standards: 50 - 150 - 300 - 600**

| | | | Ion Concentration | | | |
|---|---|---|---|---|---|---|
| Water Sample | Operator | Measurement | 40 ppm | 100 ppm | 200 ppm | 400 ppm |
| Turbid | 1 | 1 | 75 | 50 | 125 | 450 |
| | | 2 | <50 | 50 | 100 | 550 |
| | 2 | 1 | 150 | 100 | 200 | 600 |
| | | 2 | 100 | 100 | 200 | 600 |
| | 3 | 1 | 125 | 140 | 225 | 320 |
| | | 2 | 100 | 120 | 275 | 400 |
| High TDS | 1 | 1 | 125 | 100 | 75 | 250 |
| | | 2 | 125 | 100 | 200 | 300 |
| | 2 | 1 | 100 | 100 | 200 | 600 |
| | | 2 | 100 | 200 | 150 | 600 |
| | 3 | 1 | 150(80) | 75 | 180 | 650 |
| | | 2 | 150(60) | 200 | 225 | 650 |
| Colored | 1 | 1 | 75 | 50 | 300 | 600 |
| | | 2 | 50 | 100 | 75 | 600 |
| | 2 | 1 | 300(100) | 150 | 200 | 700 |
| | | 2 | 100 | 150 | 150 | 700 |
| | 3 | 1 | 125 | 160 | 225 | 550 |
| | | 2 | 140 | 150 | 400 | 600 |
| Well | 1 | 1 | 50 | 60 | 200 | 400 |
| | | 2 | 40 | 75 | 150 | 600 |
| | 2 | 1 | 100 | 150 | 200 | 600 |
| | | 2 | 100 | 75 | 150 | 700 |
| | 3 | 1 | 100 | 130 | 325 | 500 |
| | | 2 | 100 | 75 | 250 | 500 |
| Organically Polluted | 1 | 1 | 300(50) | 150 | 150 | 225 |
| | | 2 | 250(100) | 50 | 100 | 600 |
| | 2 | 1 | 100 | 100 | 150 | 600 |
| | | 2 | 150 | 150 | 150 | 600 |
| | 3 | 1 | 100 | 140 | 225 | 620 |
| | | 2 | 125 | 125 | 300 | 600 |

## TABLE 45. Magnesium - Blank Tests (ppm)

(All samples consisted of deionized water)

| Operator 1 | Operator 2 | Operator 3 |
|---|---|---|
| Blank | Blank | 40 |
| Blank | Blank | 10 |
| Blank | Blank | 5 |
| Blank | Blank | 5 |
| Blank | Blank | 5 |
| Blank | Blank | 5 |
| Blank | Blank | 10 |
| Blank | Blank | 5 |
| Blank | Blank | 5 |
| Blank | Blank | 10 |
| Blank | Blank | 10 |
| Blank | Blank | 10 |
| Blank | Blank | 10 |
| Blank | Blank | 5 |
| Blank | Blank | 30 |

## TABLE 46. Analysis of Qualifications Tests - Magnesium Ion (Refer to Section 4.4 for explanation of terms)

### Analysis of Variance - All Ion Concentrations

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 122,697.917 | 2 | 61,348.958 | 17.121** |
| Ion Level | 389,217.500 | 3 | 129,739.167 | 5.834* |
| Water Sample | 55,814.583 | 4 | 13,953.646 | 3.568 |
| OPXIONLEV | 133,428.750 | 6 | 22,238.125 | 6.206** |
| OPXWATSAM | 31,285.417 | 8 | 3,910.677 | 1.091 |
| WATSMXIONL | 71,680.417 | 12 | 5,973.368 | 1.667 |
| Precision | 215,000.00 | 60 | 3,583.333 | |

$S_p^2 = 3,583$

$S_o^2 = 1,444$

Third Order Interaction

MS = 9034

### Average Errors of Measurement
(Measured Ion Concentration Minus Actual Ion Concentration)

| | Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| **Operator** | 40 | 100 | 200 | 400 |
| 1 | 71.50 | -21.50 | -50.00 | 47.50 |
| 2 | 90.00 | 27.50 | -25.00 | 230.00 |
| 3 | 81.50 | 31.50 | 63.00 | 139.00 |
| **Water Sample** | | | | |
| Turbid | 55.83 | -6.67 | -8.33 | 70.00 |
| High TDS | 85.00 | 29.17 | -28.33 | 108.33 |
| Colored | 91.67 | 26.67 | 25.00 | 225.00 |
| Well | 41.67 | -5.83 | 12.50 | 150.00 |
| Organically Polluted | 130.83 | 19.17 | -20.83 | 140.83 |

| | Operator | | |
|---|---|---|---|
| **Water Sample** | 1 | 2 | 3 |
| Turbid | -16.25 | 71.25 | 28.13 |
| High TDS | -25.63 | 71.25 | 100.00 |
| Colored | 46.25 | 121.25 | 108.75 |
| Well | 11.88 | 74.38 | 62.50 |
| Organically Polluted | 43.13 | 65.00 | 94.38 |

## TABLE 46.(Continued)

## Analysis of Variance for Each Ion Concentration

The ion concentration is 40 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 1,715.000 | 2 | 857.500 | 0.493 |
| Water Sample | 28,761.667 | 4 | 7,190.417 | 0.915 |
| OPXWATSAM | 62,893.333 | 8 | 7,861.667 | 4.518** |
| Precision | 26,100.000 | 15 | 1,740.00 | |

$s_p^2 = 1,740$

$s_o^2 = 0$ (1

$\underline{\overline{X}} = 121.000$

The ion concentration is 100 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 17,420.000 | 2 | 8,710.000 | 5.203* |
| Water Sample | 7,358.333 | 4 | 1,839.583 | 4.533* |
| OPXWATSAM | 3,246.667 | 8 | 405.833 | 0.242 |
| Precision | 25,112.500 | 15 | 1,674.167 | |

$s_p^2 = 1,674$

$s_o^2 = 704$

$\underline{\overline{X}} = 112.500$

The ion concentration is 200 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 70,460.000 | 2 | 35,230.000 | 8.445** |
| Water Sample | 12,045.000 | 4 | 3,011.250 | 2.172 |
| OPXWATSAM | 11,090.000 | 8 | 1,386.250 | 0.332 |
| Precision | 62,575.000 | 15 | 4,171.667 | |

$s_p^2 = 4,172$

$s_o^2 = 3,106$

$\underline{\overline{X}} = 196.000$

The ion concentration is 400 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 166,531.667 | 2 | 83,265.833 | 12.340** |
| Water Sample | 79,330.000 | 4 | 19,832.500 | 1.023 |
| OPXWATSAM | 155,110.000 | 8 | 19,388.750 | 2.873 |
| Precision | 101,212.500 | 15 | 6,747.500 | |

$s_p^2 = 6,748$

$s_o^2 = 7,652$

$\underline{\overline{X}} = 538.833$

---

(1) If the F value for operator effect is not significant, $s_o^2$ is considered to be zero.

TABLE 46. (Continued)

## Average Errors for Individual Factors

| Operator | Average Error |
|---|---|
| 1 | 11.875 |
| 2 | 80.625 |
| 3 | 78.750 |
| **Water Sample** | |
| Turbid | 27.708 |
| High TDS | 48.542 |
| Colored | 92.083 |
| Well | 49.583 |
| Organically Polluted | 67.500 |
| **Ion Concentration** | |
| 40 ppm | 81.000 |
| 100 ppm | 12.500 |
| 200 ppm | -4.000 |
| 400 ppm | 138.833 |

**Figure 9. Magnesium Rings**

No false positives greater than or equal to the lowest standard concentration were found in the blank tests. Thus, there were no significant false positives. Insignificant false positives were found 33% of the time.

Referring to the method suggested in Section 4.4.4 (p. 38) for use of the ring oven for screening, we see that it would appear to work fairly well for this case, even though several of the measurements have large errors. The results at each ion concentration for the 15 pairs of measurements are given in Table 47. When the ion concentration is far from 150 ppm (the critical level) we do quite well, and even when the ion concentration is slightly greater than the 150 ppm concentration, we also do quite well, making only one mistake. Note again that these are rather tentative conclusions as discussed in Section 4.4.4. Figure 10 illustrates the general screening analysis graphically. It can be seen from this figure that at the 400 ppm concentration, no incorrect "go-no go" decisions as to water potability were made. At the 200 ppm concentration, over 80% of the potability decisions were also made correctly.

## Investigation of Erratic Results

In an attempt to identify the cause of the high results at the lowest level of ion concentration, some limited laboratory tests were performed. It was noted during the qualifications testing that white particles were observed in the magnesium solutions which gave high results at the 40 ppm concentration. These particles were found in both natural water samples and in simulated water samples prepared with deionized water. In the case of the sample prepared with deionized water, at least, these particles were not observed until the samples had aged for a period of time. It seemed likely that such particles, if they contained a high amount of Mg, could be the cause of high sample measurements since particles of this type could be pulled up into the pipet erratically. If these particles were deposited on the filter paper and subjected to an acid wash, then the high localized concentration of the acid could redissolve the magnesium-containing particles. This, in turn, would lead to a large increase in magnesium concentration in the ring zone, and high results. In an attempt to determine the nature of these particles and their effects on the Mg test, several laboratory experiments were conducted. Some of these experiments and their results are described in Table 48.

TABLE 47. Distribution of Replicate Results Around Decision Level for Magnesium Qualifications Tests
Decision Concentration - 150 ppm

| | Sample Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| Ring Oven Results | 40 | 100 | 200 | 400 |
| Both values ≥ 150(1) | 2 | 2 | 11 | 15 |
| Both values < 150(2) | 10 | 8 | 1 | 0 |
| Other(3) | 3 | 5 | 3 | 0 |

(1) The ion concentration is deemed unacceptable.

(2) The ion concentration is deemed acceptable

(3) More measurement is required before a decision can be made.

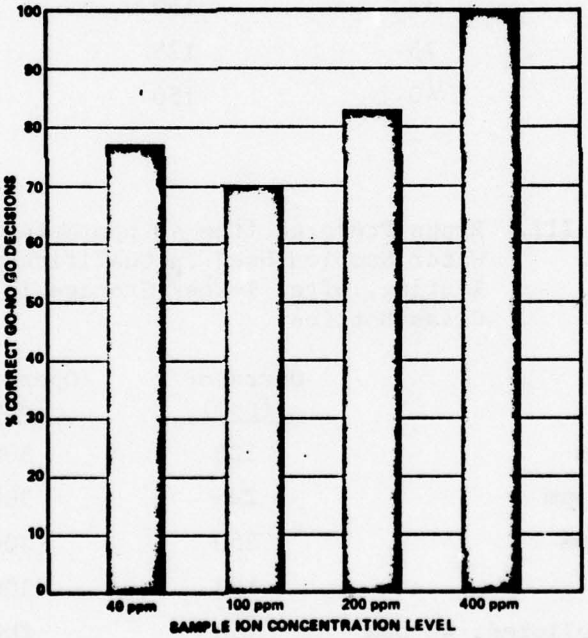


Figure 10. Percent Correct "Go-No Go" Decisions for Magnesium (Based on a decision concentration of 150 ppm)

## TABLE 48. Examination of Erratic Magnesium Results

### (a) Fresh Solutions vs. Aged Solutions

| I. Rings prepared from fresh 40 ppm Mg Standard | | II. Rings prepared using 5-day old 40 ppm Mg | |
|---|---|---|---|
| Operator 1 (ppm) | Operator 2 (ppm) | Operator 1 (ppm) | Operator 2 (ppm) |
| 50 | 40 | 250 | 125 |
| 30 | 50 | 175 | 200 |
| 75 | 40 | 175 | 200 |
| 50 | 40 | 125 | 75 |
| 50 | 30 | 250 | 100 |
| 100 | 40 | 200 | 250 |
| 20 | 40 | 200 | 125 |
| 40 | 30 | 150 | 225 |
| 75 | 75 | 125 | 100 |
| 50 | 40 | 150 | - |
| 40 | - | | |

III. Rings Prepared from 40 ppm Natural Water Samples Used in Qualifications Testing, after 1-Week Storage in Glass Bottles

| Sample | Operator 1 (ppm) | Operator 2 (ppm) | Operator 3 (ppm) |
|---|---|---|---|
| Turbid, 40 ppm | 125 | 300 | 575 |
| High TDS, 40 ppm | 225 | 300 | 175 |
| Colored, 40 ppm | 250 | 300 | 250 |
| Well, 40 ppm | 150 | 300 | 75 |
| Organically Polluted, 40 ppm | 50 | 200 | 130 |

From the results in the above table, it can be seen that rings prepared from fresh solutions gave more correct results than those prepared from solutions aged for several days.

## (b) Tests Using Two Different Primary Standard Solutions

I. Rings prepared from fresh 50 ppm Standards
A = 50 ppm from Primary Standard I
B = 50 ppm from Primary Standard II

| A | | B | |
|---|---|---|---|
| Operator 1 (ppm) | Operator 2 (ppm) | Operator 1 (ppm) | Operator 2 (ppm) |
| 100 | 100 | 200 | 125 |
| 150 | 75 | 150 | 175 |
| 150 | 125 | 150 | 200 |
| 200 | 60 | 150 | 100 |
| 150 | 75 | | 100 |

II. Rings prepared 8/25 from:
A = 50 ppm Mg, prepared 8/19 from Primary Standard I
B = 50 ppm Mg, prepared 8/19 from Primary Standard II

| A | | B | |
|---|---|---|---|
| Operator 1 (ppm) | Operator 2 (ppm) | Operator 1 (ppm) | Operator 2 (ppm) |
| 150 | 60 | 200 | 60 |
| 75 | 125 | 50 | 75 |
| 125 | 100 | 200 | 125 |
| 60 | 75 | 60 | 60 |

These results show that no difference was found between two different primary standard solutions of 1000 ppm magnesium used to prepare 40 ppm solutions.

## (c) Effect of Reagent Solution Age

Rings prepared on 8/31 using 40 ppm Mg made on 8/30 and treated with Magneson A prepared 8/30, and Magneson B, prepared 8/31

| Magneson A Operator 1 (ppm) | Magneson B Operator 1 (ppm) |
|---|---|
| 175 | 125 |
| | 150 |

It can be seen that age of reagent solution had no effect on high results.

### (d) Possible Leaching of Magnesium from Glassware

Blank solutions prepared 8/30, run on 8/31. Blanks consisted of deionized water adjusted with concentrated $HNO_3$ to the same pH as a fresh 40 ppm Mg solution prepared simultaneously. Blank solution was stored in glass volumetric identical to those used to prepare standards.

| Operator 1 (ppm) |
|---|
| 2 |
| 5 |
| 2 |
| 5 |
| 3 |

As shown by the above data, the problem does not appear to result from leaching of magnesium from glassware, since blanks with a pH value identical to the samples gave the correct readings.

---

### (e) Samples Prepared with Distilled Water

Rings prepared on 8/31 and 9/1 from same 40 ppm Mg solution prepared 8/31 using distilled water rather than deionized water.

| 8/31, Operator 1 (ppm) | 9/1, Operator 1 (ppm) |
|---|---|
| 75 | 150 |
| 50 | 175 |
| 50 | 50 |
|  | 100 |
|  | 75 |
|  | 125 |

**These experiments demonstrated that samples prepared with distilled water gave similar readings to those prepared with deionized water.**

An attempt was also made to collect enough of these particles for an x-ray diffraction (XRD) analysis. Solutions were filtered through a 4.5μ filter, and examined using XRD. No spectra was obtained, indicating that either the substance was amorphous, or that not enough was present on the filter for the instrument's sensitivity to detect it.

In light of the observation given in Table 48 that fresh samples generally give lower results than aged samples, it appeared that either a biological growth was occurring in the samples, or that a precipitate containing magnesium was forming with time, thus leading to deposition of these Mg-containing particles onto the filter papers followed by release of relatively large amounts of magnesium when acid was applied at elevated temperatures. The low pH of the samples makes the possible formation of a precipitate seem remote; however, some acid-insoluble magnesium compounds do exist. The deionized and distilled waters are not sterile, nor, as is obvious, are the natural water samples used. Either of these processes (precipitation or biological growth) may be responsible for the high results at the low magnesium concentration. Constraints of time, however, prevented the final resolution of the true cause during this contract period.

### Conclusions

The ring oven test for magnesium using p-nitrobenzene-azo-resorcinol was found to be suitable as a general screening tool for determining water potability. The technique was able to place samples of varying concentrations on the correct side of the decision level in most cases. A tendency for samples to give high readings appeared to be due to some chemical or biological action within the samples themselves, which hindered preparation of samples of accurately known concentration, but was not due to inaccuracies in the method. The fractional factorial tests showed significant effects due to reagent temperature and age, ion concentration, and to the interaction between reagent age and ion concentration.

### 5.1.4 Calcium

The reagent selected for ring oven determination of calcium was glyoxal-bis(hydroxanil). While this reagent will react with many metals, the use of an ammonium carbonate solution will prevent all but cerium and the anion phosphate, from reacting. For more information concerning the specificity of this reagent, see reference (1). The original range evaluated for this reagent was from 10 to 20,000 ppm calcium, with standards of 10, 100, 500, 1,000, 5,000, 10,000, and 20,000 ppm.

## Procedure Adjustment

The calcium test was modified somewhat in order to increase ring gradation. Modifications consisted of elimination of heavy background by changing the tap water rinse of the filter as used during initial procedure development to a deionized water bath. Also, the final ring has been reduced from 22 mm to 14 mm, in order to increase ion concentration. The procedure used for all subsequent calcium testing is given in Appendix C.

## Operator Variability Tests

Initial standard values to be used were 50, 250, 350 and 450 ppm calcium. Tests by the operators, however, to develop technique showed that too much difficulty in differentiating between the 350 and 450 ppm standards existed. For this reason, it was decided to drop the 350 ppm standard, at least for the initial testing.

The first samples analyzed, the results of which are given in Table 49, were unsatisfactory. As 30 μl samples were used for this set (Run No. 1), it was decided to try to increase reliability by using larger sample sizes; in this case, 50 μl. Nineteen samples were analyzed in two groups, using as standards different sectors of one set of standard rings. This proved necessary because of the short-lived nature of Ca rings. In addition, an attempt was made to add a standard of 650 ppm Ca at the upper end. This proved unsuccessful, as 450 appears to be the upper reagent limit when 50 μl samples are used. The results of the second run are given in Table 50.

The standards submitted to the Army for approval for use as permanent standards were 50, 250 and 450 ppm. These standards met with approval and were used for all subsequent testing.

## Fractional Factorial Tests

The results of the fractional factorial tests for the calcium ion

TABLE 49. Operator Variability Tests - Calcium, Run No. 1

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| H | 450 | >450 | 450 |
| K | 250 | 450 | 100 |
| A | 50 | 250 | 50 |
| L | 450 | >450 | - |
| C | 250 | >450 | 450 |
| M | 50 | 250 | <50 |
| N | 350 | >450 | - |
| J | 350 | 450 | 350 |
| S | 350 | 450 | 300 |
| T | 450 | >450 | 300 |
| G | Blank | - | <50 |
| F | 350 | - | 400 |

30 µl Samples

Standards: 50-250-450

Decision Level: 250 ppm

TABLE 50. Operator Variability Tests - Calcium, Run No. 2

| **Sample** | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| A | 50 | <50 | <50 |
| B | 450 | 450 | >450 |
| C | 250 | 450 | 200 |
| D | 250 | 250 | 200 |
| E | 350 | >450 | 250 |
| F | 350 | >450 | 276 |
| G | Blank | 200 | <50 |
| H | 450 | >450 | >450 |
| I | 250 | >450 | 200 |
| J | 350 | 450 | 450 |
| L | 450 | 450 | 250 |
| M | 50 | 60 | <50 |
| N | 350 | 450 | 250 |
| P | 250 | 250 | 300 |
| P | Blank | <50 | <50 |
| Q | 450 | 450 | <50 |
| R | 250 | 250 | 400 |
| S | 350 | 250 | 250 |
| T | 450 | 300 | 250 |

50 µl Samples

Standards: 50-250-450

Decision Level: 250 ppm

are given in Table 51, while Figure 11 represents this data graphically. Tables 52(a), 52(b) and 52(c) give the statistical analysis of these results. As can be seen from the data for all observations in Table 52(a), highly significant results (indicated by double stars) were seen with variation in reagent age and ion concentration. It is observed from the graph given as Figure 11, that many of the 450 ppm Ca samples gave a reading of 250 ppm. This may be due in part to reagent age, which had a highly significant effect. The ion concentration effect is only critical at the high ion concentration, however, and this is demonstrated by the fact that no significant effects whatever are seen for the low ion concentration. In addition, the low ion concentration exhibits a lesser average error.

It is observed from Table 51 that the problem at the high ion level is due to low results. This may be caused by the sample size, in that the pipets used required multiple applications in order to reach 50 µl. When a number of samples are run consecutively, requiring a number of repetitive actions, operator attention can wander. This causes errors which should not occur when only one or two samples are run, such as in a field situation. In addition, 600 ppm is above the saturation point of the reagent; that is, above the linear portion of the curve of color intensity versus concentration. For samples in this non-linear area, smaller sample sizes than 50 µl should be used. Table 53 summarizes the results for the statistical analysis of the fractional factorial tests.

## Qualifications Tests

Table 54 gives the results for the qualifications testing of calcium, while the data from the blank tests for calcium are shown in Table 55. The statistical evaluation of the qualifications testing data is given in Table 56. Figure 12 shows the permanent standard rings used in the calcium qualifications testing.

For this ion, the standards were 50, 250 and 400 and the ion concentrations were 50, 175, 350 and 600 ppm. The data seems reasonably consistent except that when the ion concentration was 600 ppm, the measured value was generally much lower. This tended to indicate that between 400 and 600 ppm Ca, the saturation point of the reagent was reached. This is to be expected since the maximum sample size of 50 µl was used. At values above 400 ppm, smaller samples may be necessary.

## TABLE 51. Results of Calcium Fractional Factorial Tests (Refer to Table 11, p. 26, for actual sample content)

| Sample No. | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 50 | <50 | 50 |
| b | 50 | 50 | 50 |
| c | 50 | <50 | 50 |
| d | 50 | <50 | 450 |
| e | 50 | 75 | 50 |
| f | 600 | 450 | 300 |
| g | 50 | <50 | 50 |
| h | 50 | <50 | 50 |
| i | 600 | 300 | 450 |
| j | 600 | 450 | 250 |
| k | 50 | <50 | <50 |
| l | 600 | 100 | 125 |
| m | 600 | 250 | 400 |
| n | 50 | 50 | 50 |
| o | 50 | 50 | 50 |
| p | 600 | 450 | 450 |
| q | 50 | <50 | 50 |
| r | 600 | 250 | 250 |
| s | 600 | 250 | 250 |
| t | 600 | 250 | 250 |
| u | 50 | <50 | <50 |
| v | 50 | <50 | <50 |
| w | 600 | 400 | 450 |
| x | 50 | 50 | 50 |
| y | 600 | 250 | 250 |
| z | 50 | <50 | <50 |
| aa | 600 | 300 | 450 |
| bb | 50 | <50 | <50 |
| cc | 600 | 450 | 450 |
| dd | 600 | 300 | 450 |
| ee | 600 | 200 | 250 |
| ff | 600 | 250 | 250 |

Standards: 50 - 250 - 450
Operator No. 4
Decision Concentration: 150 ppm

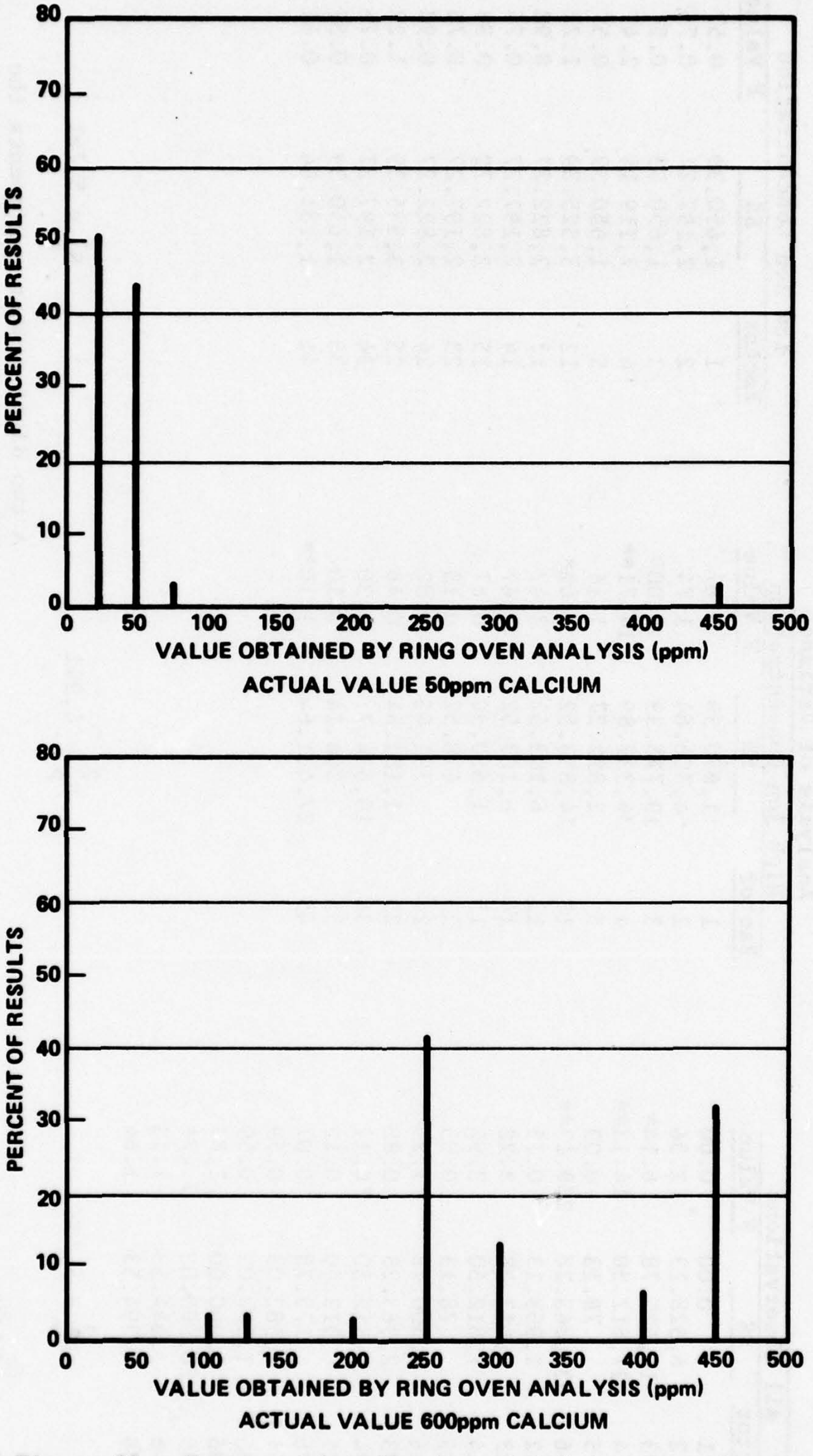


Figure 11. Percent Distribution of Calcium Fractional Factorial Test Results at Tested Ion Concentrations

TABLE 52(a). Statistical Analysis of Calcium Fractional Factorial Tests

$S_p^2/2$ used for residual **mean** square

**Analysis of Variance**

| **All Observations** | | | High Ion Concentration | | | Low Ion Concentration | | |
|---|---|---|---|---|---|---|---|---|
| **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** |
| 1 | 0.00 | 0.00 | 1 | 1,650.39 | 0.67 | 1 | 1,650.39 | 0.57 |
| 2 | 6,328.13 | 2.36 | 2 | 4,306.64 | 1.74 | 2 | 2,197.27 | 0.76 |
| 3 | 16,425.78 | 6.14* | 3 | 19,775.39 | 8.00* | 3 | 1,650.39 | 0.57 |
| 4 | 37,812.50 | 14.13** | 4 | 36,337.89 | 14.71** | 4 | 7,119.14 | 2.47 |
| 5 | 78.13 | 0.03 | 5 | 2,822.27 | 1.14 | 5 | 1,650.39 | 0.57 |
| 6 | 639,863.28 | 239.13** | 12 | 14,853.52 | 6.01* | 12 | 3,525.39 | 1.22 |
| 12 | 1,953.13 | 0.73 | 13 | 6,103.52 | 2.47 | 13 | 2,822.27 | 0.98 |
| 13 | 8,613.28 | 3.22 | 14 | 6,103.52 | 2.47 | 14 | 2,197.27 | 0.76 |
| 14 | 7,812.50 | 2.92 | 15 | 1,650.30 | 0.67 | 15 | 2,822.72 | 0.98 |
| 15 | 78.13 | 0.03 | 23 | 478.52 | 0.13 | 23 | 2,197.27 | 0.76 |
| 16 | 3,300.78 | 1.23 | 24 | 791.02 | 0.82 | 24 | 2,822.27 | 0.98 |
| 23 | 2,363.28 | 0.88 | 25 | 1,181.64 | 0.48 | 25 | 3,525.39 | 1.22 |
| 24 | 312.50 | 0.12 | 34 | 10,634.77 | 4.30 | 34 | 2,197.27 | 0.76 |
| 25 | 312.50 | 0.12 | 35 | 244.14 | 0.10 | 35 | 1,650.39 | 0.57 |
| 26 | 175.78 | 0.07 | 45 | 27,431.64 | 11.10** | 45 | 1,181.64 | 0.41 |
| 34 | 1,582.03 | 0.59 | | | | | | |
| 35 | 1,582.03 | 0.59 | | | | | | |
| 36 | 5,000.00 | 1.87 | | | | | | |
| 45 | 20,000.00 | 7.47* | | | | | | |
| 46 | 5,644.53 | 1.13 | | | | | | |
| 56 | 4,394.53 | 1.64 | | | | | | |
| | $S_p^2 = 5{,}352$ | | | $S_p^2 = 4{,}941$ | | | $S_p^2 = 5{,}761$ | |

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 52(b). Statistical Analysis of Calcium Fractional Factorial Tests

### Analysis of Variance - All Observations

Residual Mean Square = 4,980.47†

| Factor | SS | F Value |
|---|---|---|
| 1 | 0.00 | 0.00 |
| 2 | 6,328.13 | 1.27 |
| 3 | 16,425.78 | 3.30 |
| 4 | 37,812.50 | 7.59* |
| 5 | 78.13 | 0.02 |
| 6 | 639,863.28 | 128.47** |
| 12 | 1,953.13 | 0.39 |
| 13 | 8,613.28 | 1.73 |
| 14 | 7,812.50 | 1.57 |
| 15 | 78.13 | 0.02 |
| 16 | 3,300.78 | 0.66 |
| 23 | 2,363.28 | 0.47 |
| 24 | 312.50 | 0.06 |
| 25 | 312.50 | 0.06 |
| 26 | 175.78 | 0.04 |
| 34 | 1,582.03 | 0.32 |
| 35 | 1,582.03 | 0.32 |
| 36 | 5,000.00 | 1.00 |
| 45 | 20,000.00 | 4.02 |
| 46 | 5,644.53 | 1.13 |
| 56 | 4,394.53 | 0.88 |

†For this table, the lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

TABLE 52(c). Statistical Analysis of Calcium Fractional Factorial Tests

The Average Errors for the High and Low Levels of Each Factor Are:

|  | High | Low |
|---|---|---|
| 1 | -140.625 | -140.625 |
| 2 | -126.563 | -154.688 |
| 3 | -117.969 | -163.281 |
| 4 | -175.000 | -106.250 |
| 5 | -139.063 | -142.188 |
| 6 | -282.031 | 0.781 |

(All observations)

|  | High | Low |
|---|---|---|
| 1 | -271.875 | -292.188 |
| 2 | -265.625 | -298.438 |
| 3 | -246.875 | -317.188 |
| 4 | -329.688 | -234.375 |
| 5 | -268.750 | -295.313 |

(At the high ion concentration)

|  | High | Low |
|---|---|---|
| 1 | -9.375 | 10.938 |
| 2 | 12.500 | -10.938 |
| 3 | 10.938 | -9.375 |
| 4 | -20.313 | 21.875 |
| 5 | -9.375 | 10.938 |

(At the low ion concentration)

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

TABLE 53. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Calcium

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | - | - | - | - | - | - |
| Color | - | - | - | - | - | - |
| Detection Reagent Temperature | - | - | * | - | - | - |
| Reagent Age | - | - | - | ** | * | - |
| Chlorine Concentration | - | - | - | * | - | - |
| Ion Concentration | - | - | - | - | - | ** |

- = no significant effect
* = significant effect
** = highly significant effect

## TABLE 54. Calcium Qualifications Tests

Standards: 50 - 250 - 450

| Water Sample | Operator | Measurement | Ion Concentration<br>50 ppm | 175 ppm | 350 ppm | 600 ppm |
|---|---|---|---|---|---|---|
| Turbid | 1 | 1 | 40 | 250 | 250 | 450 |
| | | 2 | 40 | 150 | 300 | 350 |
| | 2 | 1 | 50 | 300 | 450 | 700 |
| | | 2 | 50 | 350 | 450 | 500 |
| | 3 | 1 | 50 | 250 | 275 | 375 |
| | | 2 | 60 | 225 | 350 | 450 |
| High TDS | 1 | 1 | 30 | 125 | 450 | 450 |
| | | 2 | 30 | 200 | 200 | 400 |
| | 2 | 1 | 10 | 150 | 400 | 350 |
| | | 2 | 10 | 250 | 500 | 400 |
| | 3 | 1 | 40 | 400 | 300 | 300 |
| | | 2 | 40 | 250 | 400 | 400 |
| Colored | 1 | 1 | 40 | 100 | 250 | 300 |
| | | 2 | 30 | 250 | 250 | 400 |
| | 2 | 1 | 20 | 100 | 200 | 450 |
| | | 2 | 50 | 250 | 400 | 350 |
| | 3 | 1 | 40 | 300 | 350 | 350 |
| | | 2 | 50 | 275 | 370 | 500 |
| Well | 1 | 1 | 30 | 250 | 300 | 550 |
| | | 2 | 30 | 250 | 250 | 450 |
| | 2 | 1 | 50 | 150 | 450 | 450 |
| | | 2 | 50 | 75 | 350 | 250 |
| | 3 | 1 | 50 | 175 | 200 | 200 |
| | | 2 | 40 | 230 | 375 | 400 |
| Organically Polluted | 1 | 1 | 50 | 250 | 350 | 450 |
| | | 2 | 10 | 125 | 250 | 200 |
| | 2 | 1 | 10 | 250 | 250 | 400 |
| | | 2 | 30 | 200 | 500 | 350 |
| | 3 | 1 | 40 | 200 | 275 | 500 |
| | | 2 | 40 | 100 | 350 | 475 |

TABLE 55. Calcium - Blank Tests (ppm)

(All samples consisted of deionized water)

| Operator 1 | Operator 2 | Operator 3 |
|---|---|---|
| Blank | 10 | 5 |
| Blank | 10 | 5 |
| Blank | 20 | 10 |
| Blank | 40 | 10 |
| Blank | 50 | 10 |
| Blank | 10 | 5 |
| Blank | 10 | 20 |
| Blank | 100 | 10 |
| Blank | 20 | 10 |
| Blank | 10 | 5 |
| Blank | 10 | 20 |
| Blank | 30 | 5 |
| Blank | 40 | 5 |
| Blank | 10 | 20 |
| Blank | 50 | 10 |

TABLE 56. Analysis of Qualifications Tests - Calcium Ion
(Refer to Section 4.4 for explanation of terms)

Analysis of Variance - All Ion Concenteations

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 23,050.417 | 2 | 11,525.208 | 2.102 |
| Ion Level | 928,865.625 | 3 | 309,621.875 | 32.824** |
| Water Sample | 30,811.667 | 4 | 7,702.917 | 0.734 |
| OPXIONLEV | 56,596.250 | 6 | 9,432.708 | 1.720 |
| OPXWATSAM | 83,905.833 | 8 | 10,488.229 | 1.913 |
| WATSMXIONL | 34,575.000 | 12 | 2,881.250 | 0.525 |
| Precision | 328,987.500 | 60 | 5,483.125 | |

$S_p^2 = 5,483$

$S_o^2 = (151)$ (1)

Third Order Interaction

MS = 5,712

Average Errors of Measurement
(Measured Ion Concentration Minus Actual Ion Concentration)

| | Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| **Operator** | 50 | 175 | 350 | 600 |
| 1 | -17.00 | 20.00 | -65.00 | -200.00 |
| 2 | -17.00 | 22.50 | 45.00 | -180.00 |
| 3 | -5.00 | 65.50 | -25.50 | -205.00 |
| **Water Sample** | | | | |
| Turbid | -1.67 | 62.50 | -4.17 | -129.17 |
| High TDS | -23.33 | 54.17 | 25.00 | -216.67 |
| Colored | -11.67 | 37.50 | -46.67 | -208.33 |
| Well | -8.33 | 13.33 | -29.17 | -216.67 |
| Organically Polluted | -20.00 | 12.50 | -20.83 | -204.17 |

| | Operator | | |
|---|---|---|---|
| **Water Sample** | 1 | 2 | 3 |
| Turbid | -65.00 | 50.00 | -39.38 |
| High TDS | -58.13 | -35.00 | -27.50 |
| Colored | -91.25 | -66.25 | -14.38 |
| Well | -30.00 | -65.63 | -85.00 |
| Organically Polluted | -83.13 | -45.00 | -46.25 |

(1) If the F for the operator effect is not significant, $S_o^2$ is considered to be zero.

## TABLE 56. (Continued)

### Analysis of Variance for Each Ion Concentration

The ion concentration is 50 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 960.000 | 2 | 480.000 | 4.364* |
| Water Sample | 1,846.667 | 4 | 461.667 | 3.148 |
| OPXWATSAM | 1,173.333 | 8 | 146.667 | 1.333 |
| Precision | 1,650.000 | 15 | 110.000 | |

$S_p^2 = 110$

$S_o^2 = 37$

$\underline{\overline{X}} = 37.000$

The ion concentration is 175 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 13,085.000 | 2 | 6,542.500 | 1.469 |
| Water Sample | 12,603.333 | 4 | 3,150.833 | 0.397 |
| OPXWATSAM | 63,506.667 | 8 | 7,938.333 | 1.782 |
| Precision | 66,825.000 | 15 | 4,455.000 | |

$S_p^2 = 4,455$

$S_2^o = 0^{(1)}$

$\underline{\overline{X}} = 139.000$

The ion concentration is 350 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 62,101.667 | 2 | 31,050.833 | 3.692* |
| Water Sample | 17,728.333 | 4 | 4,432.083 | 1.318 |
| OPXWATSAM | 26,906.667 | 8 | 3,363.333 | 0.400 |
| Precision | 126,137.500 | 15 | 8,409.167 | |

$S_p^2 = 8,409$

$S_o^2 = 2,264$

$\underline{\overline{X}} = 334.833$

The ion concentration is 600 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 3,500.000 | 2 | 1,750.000 | 0.195 |
| Water Sample | 33,208.333 | 4 | 8,302.083 | 0.513 |
| OPXWATSAM | 129,416.667 | 8 | 16,177.083 | 1.806 |
| Precision | 134,375.000 | 15 | 8,958.333 | |

$S_p^2 = 8958$

$S_2^o = 0^{(1)}$

$\underline{\overline{X}} = 405$

(1) If the F value for the operator effect is not significant, $S_o^2$ is considered to be zero.

## TABLE 56. (Continued)

### Average Errors for Individual Factors

| Operator | Average Error |
|---|---|
| 1 | -65.500 |
| 2 | -32.375 |
| 3 | -42.500 |
| **Water Sample** | |
| Turbid | -18.125 |
| High TDS | -40.208 |
| Colored | -57.292 |
| Well | -60.208 |
| Organically Polluted | -58.125 |
| **Ion Concentration** | |
| 50 ppm | -13.000 |
| 175 ppm | -36.000 |
| 350 ppm | -15.967 |
| 600 ppm | -195.000 |

**Figure 12. Calcium Rings**

From the analysis of variance table, the only significant factor was the different ion concentrations, and this is probably attributable to the large errors in measuring the 600 ppm samples. The estimate of precision. $S_p^2$ is almost the same as that obtained with the fractional factorial test. Since the operator effect was not found significant, we would estimate it as zero. Using the equation given in Section 4.4.4 (p. 38), we calculate $S_o^2$ as 151. A parenthesis is put around the 151 in the table, since the best estimate would be zero. The average errors for the individual ion concentrations are the greatest at the 600 ppm level, which is to be expected, as this value is outside the linear range of the reagent when 50 μl samples are used. The average errors for the other three ion concentrations are excellent, especially when one considers the range covered by the standards (400 ppm). As can be observed from Table 55 (p. 121), no false positives exceeding the decision level occurred. Insignificant false positives were obtained 67% of the time.

At each ion concentration, 15 pairs of measurements were made. The distribution of these measurements around the decision level is shown in Table 57. Referring to the method suggested in Section 4.4.4 (p. 38) for using the ring oven as a screening method, we see that it would again appear to work fairly well. When the ion concentration is far from 250 (the critical level), we do quite well. At 50 ppm, we would have decided it was below 250 for each pair of measurements. At 600 ppm, we also would make no errors; however, when it is close (at 175 or 350 ppm) more testing would be required. Note again that these are rather tentative conclusions, as discussed in Section 4.4.4. Figure 13 graphically illustrates the results of the general screening analysis. At levels above the 250 ppm decision level, a better than 90% value for correct "go-no go" decisions was obtained.

## Conclusions

The use of the ring oven method for calcium in natural waters proved successful as a screening technique. At levels far above and far below the decision level of 250 ppm, the ring oven, in almost every case, places the sample on the correct side. In no case involving the highest and

TABLE 57. Distribution of Replicate Results Around Decision Level for Calcium Qualification Tests

Decision Concentration - 250 ppm

| | Sample Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| Ring Oven Results | 50 | 175 | 350 | 600 |
| Both Values ≥ 250 ppm$^{(1)}$ | 0 | 4 | 12 | 13 |
| Both Values < 250 ppm$^{(2)}$ | 15 | 4 | 0 | 0 |
| Other$^{(3)}$ | 0 | 7 | 3 | 2 |

(1) The ion concentration is deemed unacceptable.

(2) The ion concentration is deemed acceptable.

(3) More measurement is required before a decision can be made.

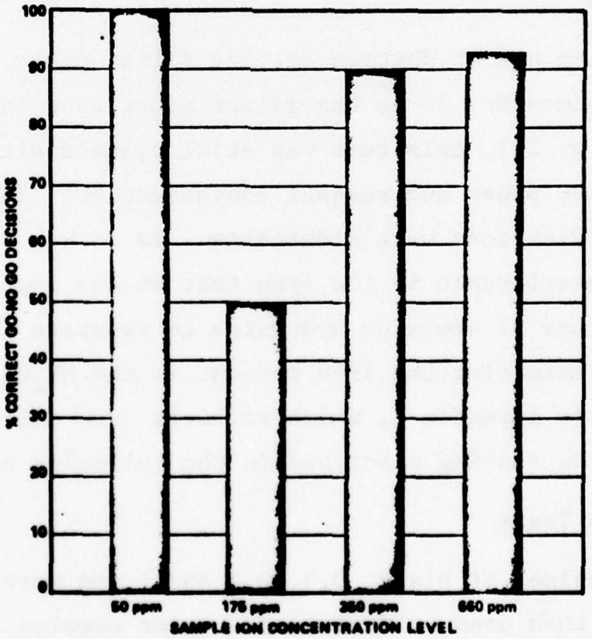


Figure 13. Percent Correct "Go-No Go" Decisions for Calcium (Based on a decision concentration of 250 ppm)

lowest levels tested were both measurements on a single sample placed on the wrong side of the decision level. At values closer to the decision value, only four instances occurred when both measurements placed a sample on the wrong side of the decision level, and these would have involved false positives, i.e., acceptable samples would have been rejected.

The test did give low results at the upper extreme of 600 ppm; however, this is above the highest standard ring concentration, and saturation has occurred. In any event, at no time was a 600 ppm sample placed below the decision value for both replicates of a sample. Factors which were found to have a large effect during fractional factorial testing were reagent age and ion concentration.

### 5.1.5 Iron

Iron was determined by the ring oven method using the reagent Ferrozine, or [3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid, disodium salt]. This reagent will also react with copper and cobalt. Ferrozine was selected for the original range of 0.1 to 10 ppm iron.

#### Procedure Adjustment

Although the use of Whatman No. 541 filter paper was a substantial improvement over Whatman No. 40 as the filter paper used in the iron test (see Section 4.1.3, p. 21), this test was still plagued with erratic results due to sporadic filter paper and reagent contamination. In order to correct this, procedure modifications were undertaken. As it was determined that copper was not an interference in the iron test at the copper decision level of 1 ppm, the use of ammonium hydroxide to separate iron from copper was discontinued, eliminating the iron present in the $NH_4OH$ solution. The procedure shown in Appendix C, which reflects this elimination of $NH_4OH$, was used in the testing described in the following sections.

#### Operator Variability Tests

Standard values of blank, 0.3, 0.5 and 1 ppm were tested for reproducibility and then used to analyze ten water samples. Table 58 gives the results, which were erratic. During the two operator sample analysis, it was observed that one operator's samples gave consistently darker rings

TABLE 58. Operator Variability Tests - Iron, Standards Prepared by Operator

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) |
|---|---|---|
| A | 0.5 | 0.5 |
| B | 0.3 | 0.9 |
| C | 0.3 | 0.5 |
| D | 1.0 | 1.0 |
| E | Blank | Blank |
| F | 0.5 | 0.3 |
| G | 0.3 | 0.3 |
| H | 1.0 | 0.6 |
| I | Blank | Blank |

15 µl samples
Standards: Blank - 0.3 - 0.5 - 1.0
Decision Level: 0.3 ppm

---

then the other operator. The only difference in the method of ring preparation were the boxes of Whatman 541 used. Tests on these boxes of filter paper showed a wide variance in iron content. Although Whatman 541 is much superior to Whatman 40, as far as Fe content, it appeared that it would require use of a pre-wash with acid. A pre-wash step was, therefore, incorporated into the procedure and the analyses repeated.

Results were still erratic, even though the No. 541 filters were first subjected to an $HNO_3$ acid wash. Table 59 shows the results of an analysis using $HNO_3$- washed filters. It appeared that the speed at which the acid was applied greatly affected the degree of iron removal. This speed was extremely difficult to control.

Attempts were also made to improve washing efficiency by using HCl rather than $HNO_3$. This proved unsuccessful, as did attempts to improve results by increasing sample size from 15 µl to 50 µl. Table 60 shows the results from these experiments.

On the basis of the above experiments, it was concluded that no advantage will be gained in accuracy by adding a preliminary wash step to

TABLE 59. Operator Variability Tests - Iron, Nitric Acid-Washed Filters

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| A | 1.0 | 0.3 | 0.5 |
| B | 0.5 | 0.7 | 1.8 |
| C | Blank | 0.7 | 0.1 |
| D | 0.5 | Blank | Blank |
| E | 1.0 | 1.0 | 0.7 |
| F | 0.2 | 1.0 | 0.1 |
| G | Blank | Blank | 1.0 |
| H | 0.2 | Blank | 0.1 |
| I | 0.5 | Blank | 0.9 |
| J | Blank | 0.2 | 2.0 |

15 µl samples
Standards: Blank - 0.3 - 0.7 - 2

---

TABLE 60. Operator Variability Tests - Iron, HCl-Washed Filters

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| Fifteen Microliter Samples and Standards | | | |
| A | 1.0 | 0.8 | 1.0 |
| B | 0.5 | 0.3 | 0.3 |
| C | Blank | Blank | 0.3 |
| D | 0.5 | Blank | Blank |
| E | 1.0 | Blank | Blank |
| Fifty Microliter Samples and Standards | | | |
| F | 0.2 | Blank | 0.3 |
| G | Blank | Blank | 0.7 |
| H | 0.2 | 0.3 | 0.7 |
| I | 0.5 | 0.6 | 1.0 |
| J | Blank | 0.3 | 0.5 |

Standards: Blank - 0.3 - 0.7 - 2

the iron test. This was substantiated by the iron test results obtained initially with unwashed filters (Table 58, p.129) and results obtained in two-operator testing shown in Table 61. Comparison of these results with those in Tables 59 and 60 (p. 130) demonstrates that no advantage is obtained when the filters are washed.

TABLE 61. Operator Variability Tests - Iron, Unwashed Filter Papers

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator #5 (ppm) | Ring Oven Results Operator #6 (ppm) |
|---|---|---|---|
| A | 1.0 | Blank | 0.5 |
| B | 0.5 | 0.7 | 0.9 |
| C | Blank | 0.3 | 1.0 |
| D | 0.5 | 0.3 | 0.7 |
| E | 1.0 | 0.2 | Blank |
| F | 0.2 | Blank | 0.3 |
| G | Blank | Blank | 0.1 |
| H | 0.3 | 0.3 | Blank |
| I | 0.5 | 0.7 | 0.7 |
| J | Blank | 0.3 | 0.9 |

15 μl samples
Standards: Blank - 0.3 - 0.7 - 2

Thus, it was decided not to wash the filter with acid prior to sample analysis. The standard values of blank, 0.3, 0.7 and 2.0 ppm were submitted to and approved by the Army for use in further testing.

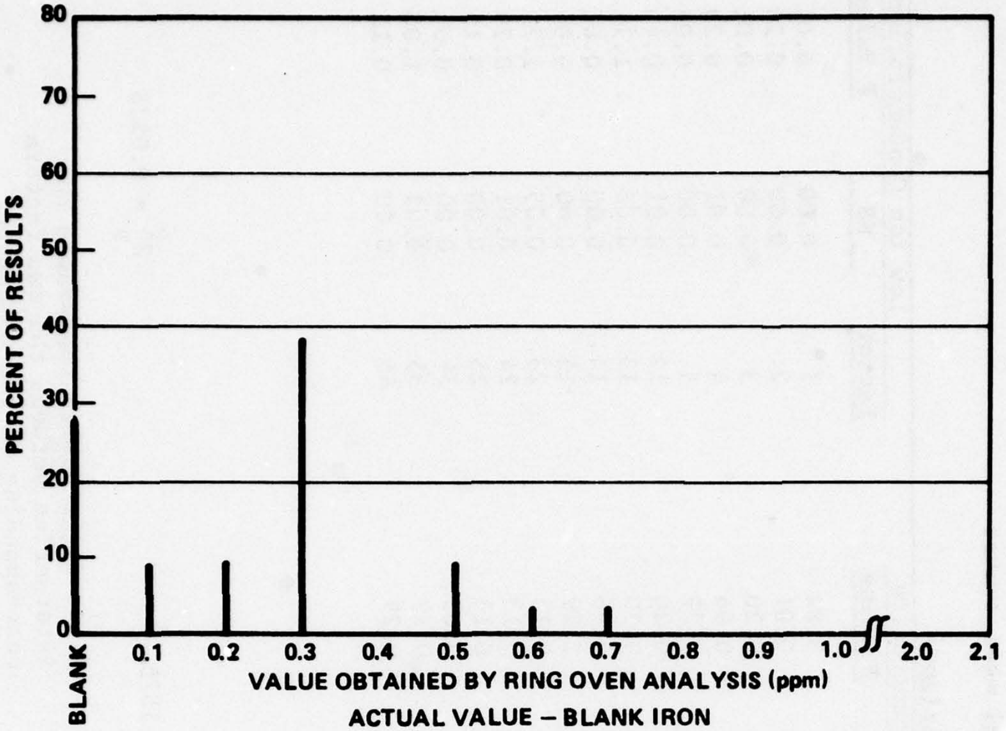
## Fractional Factorial Tests

The fractional factorial test results for the iron ion are given in Table 62 and presented graphically in Figure 14. The statistical analysis of these results are presented in Tables 63(a), (b) and (c), and summarized in Table 64. The results in Table 62 are observed to be quite erratic. At a meeting held August 10, 1977, between the Army and Atlantic Research, it was mutually decided that the test for iron in its present form was not

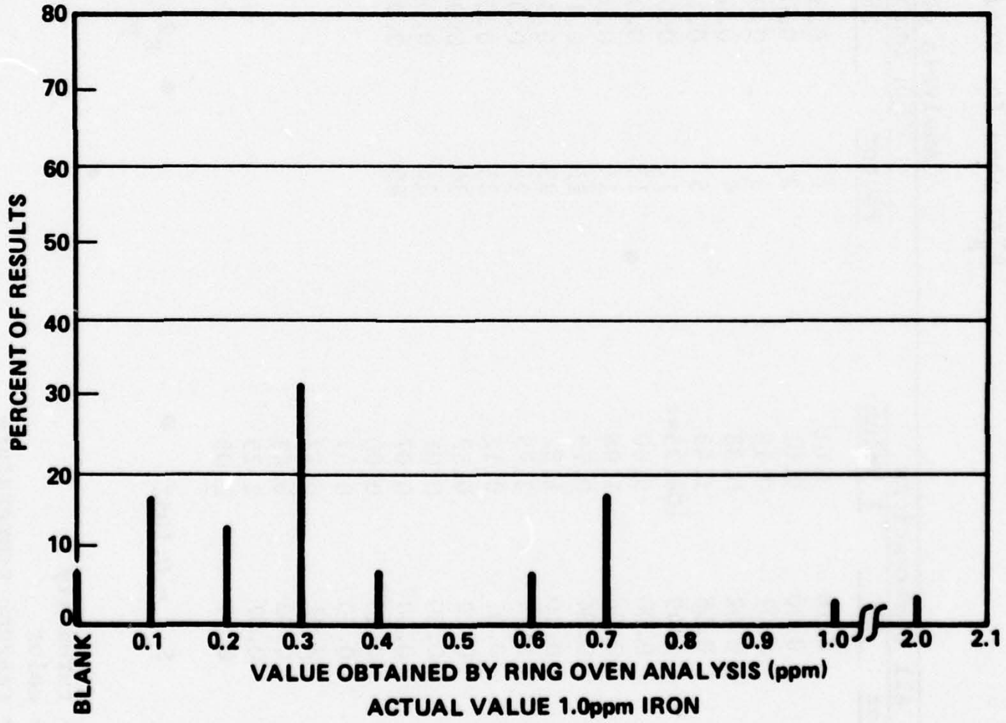
**TABLE 62. Results of Iron Fractional Factorial Tests (Refer to Table 11, p. 26, for actual sample content.)**

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | Blank | 0.3 | Blank |
| b | Blank | 0.1 | 0.2 |
| c | Blank | Blank | 0.3 |
| d | Blank | 0.5 | 0.3 |
| e | Blank | 0.7 | 0.1 |
| f | 1.0 | 0.7 | Blank |
| g | Blank | Blank | 0.5 |
| h | Blank | Blank | 0.3 |
| i | 1.0 | 0.2 | 0.2 |
| j | 1.0 | 0.3 | 0.3 |
| k | Blank | 0.2 | 0.3 |
| l | 1.0 | 0.6 | 0.6 |
| m | 1.0 | 1.0 | 0.7 |
| n | Blank | 0.3 | Blank |
| o | Blank | Blank | 0.3 |
| p | 1.0 | 2.0 | 0.1 |
| q | Blank | Blank | 0.3 |
| r | 1.0 | 0.2 | 0.1 |
| s | 1.0 | 0.3 | 0.4 |
| t | 1.0 | 0.3 | 0.3 |
| u | Blank | 0.3 | 0.1 |
| v | Blank | 0.3 | 0.3 |
| w | 1.0 | 0.1 | 0.3 |
| x | Blank | 0.2 | Blank |
| y | 1.0 | 0.7 | 0.3 |
| z | Blank | 0.5 | 0.3 |
| aa | 1.0 | 0.7 | 0.3 |
| bb | Blank | 0.6 | Blank |
| cc | 1.0 | 0.1 | 0.7 |
| dd | 1.0 | 0.4 | 0.3 |
| ee | 1.0 | 0.2 | 0.1 |
| ff | 1.0 | Blank | 0.3 |

**Standards: blank - 0.3 - 0.7 - 2**
**Operator No. 6**



ACTUAL VALUE – BLANK IRON



ACTUAL VALUE 1.0ppm IRON

Figure 14. Percent Distribution of Iron Fractional Factorial Test Results at Tested Ion Concentrations

TABLE 63(a). Statistical Analysis of Iron Fractional Factorial Tests

$S_p^2/2$ used for residual mean square

Analysis of Variance

| All Observations | | | High Ion Concentration | | | Low Ion Concentration | | |
|---|---|---|---|---|---|---|---|---|
| Factor | SS | F Value | Factor | SS | F Value | Factor | SS | F Value |
| 1 | 0.16 | 3.01 | 1 | 0.30 | 3.84 | 1 | 0.00 | 0.01 |
| 2 | 0.00 | 0.01 | 2 | 0.00 | 0.01 | 2 | 0.00 | 0.15 |
| 3 | 0.01 | 0.18 | 3 | 0.02 | 0.20 | 3 | 0.00 | 0.01 |
| 4 | 0.02 | 0.33 | 4 | 0.08 | 0.96 | 4 | 0.01 | 0.29 |
| 5 | 0.08 | 1.43 | 5 | 0.18 | 2.29 | 5 | 0.00 | 0.05 |
| 6 | 5.49 | 104.35** | 12 | 0.02 | 0.20 | 12 | 0.01 | 0.48 |
| 12 | 0.00 | 0.00 | 13 | 0.02 | 0.20 | 13 | 0.05 | 1.71 |
| 13 | 0.06 | 1.08 | 14 | 0.08 | 0.96 | 14 | 0.00 | 0.01 |
| 14 | 0.04 | 0.79 | 15 | 0.18 | 2.29 | 15 | 0.00 | 0.01 |
| 15 | 0.10 | 1.82 | 23 | 0.01 | 0.13 | 23 | 0.05 | 1.71 |
| 16 | 0.14 | 2.75 | 24 | 0.01 | 0.13 | 24 | 0.01 | 0.29 |
| 23 | 0.01 | 0.12 | 25 | 0.01 | 0.13 | 25 | 0.00 | 0.15 |
| 24 | 0.02 | 0.33 | 34 | 0.00 | 0.03 | 34 | 0.00 | 0.05 |
| 25 | 0.00 | 0.01 | 35 | 0.06 | 0.79 | 35 | 0.03 | 1.00 |
| 26 | 0.00 | 0.07 | 45 | 0.02 | 0.29 | 45 | 0.00 | 0.15 |
| 34 | 0.00 | 0.00 | | | | | | |
| 35 | 0.00 | 0.07 | | | | | | |
| 36 | 0.01 | 0.12 | | | | | | |
| 45 | 0.02 | 0.43 | | | | | | |
| 46 | 0.07 | 1.25 | | | | | | |
| 56 | 0.11 | 2.03 | | | | | | |

$S_p^2 = 0.1052$

$S_p^2 = 0.1575$

$S_p^2 = 0.0528$

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 63(b). Statistical Analysis of Iron Fractional Factorial Tests

### Analysis of Variance - All Observations

Residual Mean Square = 0.03064†

| Factor | SS | F Value |
|---|---|---|
| 1 | 0.16 | 5.16* |
| 2 | 0.00 | 0.02 |
| 3 | 0.01 | 0.31 |
| 4 | 0.02 | 0.57 |
| 5 | 0.08 | 2.45 |
| 6 | 5.49 | 179.05** |
| 12 | 0.00 | 0.00 |
| 13 | 0.06 | 1.86 |
| 14 | 0.04 | 1.35 |
| 15 | 0.10 | 3.12 |
| 16 | 0.14 | 4.71 |
| 23 | 0.01 | 0.21 |
| 24 | 0.02 | 0.57 |
| 25 | 0.00 | 0.02 |
| 26 | 0.00 | 0.12 |
| 34 | 0.00 | 0.00 |
| 35 | 0.00 | 0.12 |
| 36 | 0.01 | 0.21 |
| 45 | 0.02 | 0.74 |
| 46 | 0.07 | 2.14 |
| 56 | 0.11 | 3.49 |

†The lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

TABLE 63(c). Statistical Analysis of Iron Fractional Factorial Tests

The Average Errors for the High and Low Levels of Each Factor Are:
(Measured ion level minus actual ion level)

| | High | Low |
|---|---|---|
| 1 | -0.256 | -0.116 |
| 2 | -0.181 | -0.191 |
| 3 | -0.169 | -0.203 |
| 4 | -0.209 | -0.162 |
| 5 | -0.234 | -0.137 |
| 6 | 0.600 | 0.228 |

(All Observations)

| | High | Low |
|---|---|---|
| 1 | -0.737 | -0.462 |
| 2 | -0.606 | -0.594 |
| 3 | -0.569 | -0.631 |
| 4 | -0.669 | -0.531 |
| 5 | -0.706 | -0.494 |

(At High Ion Concentration)

| | High | Low |
|---|---|---|
| 1 | 0.225 | 0.231 |
| 2 | 0.244 | 0.212 |
| 3 | 0.231 | 0.225 |
| 4 | 0.250 | 0.206 |
| 5 | 0.237 | 0.219 |

(At Low Ion Concentration)

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

**TABLE 64. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Iron**

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | - | - | - | - | - | - |
| Color | - | - | - | - | - | - |
| Detection Reagent Temperature | - | - | - | - | - | - |
| Reagent Age | - | - | - | - | - | - |
| Chlorine Concentration | - | - | - | - | - | - |
| Ion Concentration | - | - | - | - | - | ** |

- = no significant effect
* = significant effect
** = highly significant effect

suitable for further qualifications testing or for preparation of permanent standards. For this reason, work on the iron test was halted, and no permanent standards were prepared.

### Conclusions

Every analysis method for iron in trace quantities, whether atomic absorption, x-ray fluroescence, or ring oven, etc., is plagued by iron contamination. Although every possible precaution was taken in order to eliminate this contamination, including prewashing filter papers and preparation of special acid wash solutions, it is apparent that this elimination cannot be accomplished totally at the present time. For this reason, then, the test will, in all probability, continue to be erratic at low values such as the 0.3 ppm Fe decision level until a satisfactory method for cleaning up reagents and filter papers can be found.

The test should be viable, however, in the event that the 0.3 ppm limit is increased; this limit, after all, represents only an aesthetic maximum. There is not a safety factor involved in raising this limit at the present time.

In addition, the Ferrozine-iron test should prove suitable as a general screening tool. During the previous contract's effort, the procedure was able to differentiate easily between 10 ppm and 1 ppm iron. In the event of the procedure's use for general screening, it would, of course, be recommended that several replicate samples be analyzed, as discussed in Section 4.4.4 (p. 38).

### 5.1.6 Lead

The lead reagent selected for ring oven testing was 1-(2-thiazolylazo)-2-naphthol (TAN). It was evaluated over the range of 0.05 to 1 ppm lead, with standards of blank, 0.05 and 1 ppm. The procedure used in the lead tests is given in Appendix C. TAN also reacts with mercury, iron, and copper. The latter two of these metals are eliminated through formation of cyanide complexes of copper and iron followed by removal by ion exchange. For more information regarding the development of this procedure, see Reference (1).

## Operator Variability Tests

Table 65 represents the results of the lead operator variability testing. As can be seen from the data in this table, the results were extremely erratic. Some undefined variable apparently can greatly affect the analysis. It was decided, however, to go ahead with the lead fractional factorial tests using the standard values of 0.01, 0.05, and 1 ppm.

## Fractional Factorial Tests

The results of the fractional factorial testing for the lead ion are presented in Table 66 and diagrammed graphically in Figure 15. Tables 67(a), (b) and (c) show the statistical evalaution of the fractional factorial tests. The statistical analysis of these results is summarized in Table 68. As with the operator variability tests, the results of the fractional factorial tests for lead were very unsatisfactory. As a result, a mutual decision was made by the Army and Atlantic Research to eliminate the ring oven/lead technique from any further consideration, including the preparation of permanent standards.

## Conclusions

At the August 10th meeting with the Army, it was decided that there was no need to continue with any further lead testing after review of the results of the fractional factorial tests. Work, therefore, on this ion was suspended.

The reason for the failure of the TAN reagent appeared to be lack of specificity and the complex procedure required to eliminate the various interferences. In addition to lead, the reagent responds to many other ions, including iron. At the levels of interest (0.05 ppm lead), it is almost impossible to effectively remove all contaminants. Furthermore, as discussed in Section 5.1.5 (p. 128), iron is a particular problem, being present in the reagents, filter papers, etc.

Lack of sensitivity is not the limiting factor, however, as at optimum conditions TAN was able to detect 0.05 ppm lead. No water test kit presently on the market has this capability. If a suitable method for

## TABLE 65. Operator Variability Tests - Lead

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| A | 0.4 | 0.5 | 0.3 |
| B | 0.07 | >1.0 (>1.0)* | 0.5 (>1.0) |
| C | 0.02 | >1.0 (>1.0) | >5.0 (0.02) |
| D | 0.4 | > 1.0 | 0.3 |
| E | 1.1 | >1.0 (>1.0) | 1.0 |
| F | 0.4 | 0.01 (1.7) | 0.08 (0.05) |
| G | 0.07 | 0.05 | 0.08 |
| H | 1.1 | >1.0 | 0.08 (>1.0) |
| I | 0.02 | >1.0 (1.0) | 1.0 (>1.0) |
| J | 1.1 | >1.0 | 1.0 |

50 µl samples

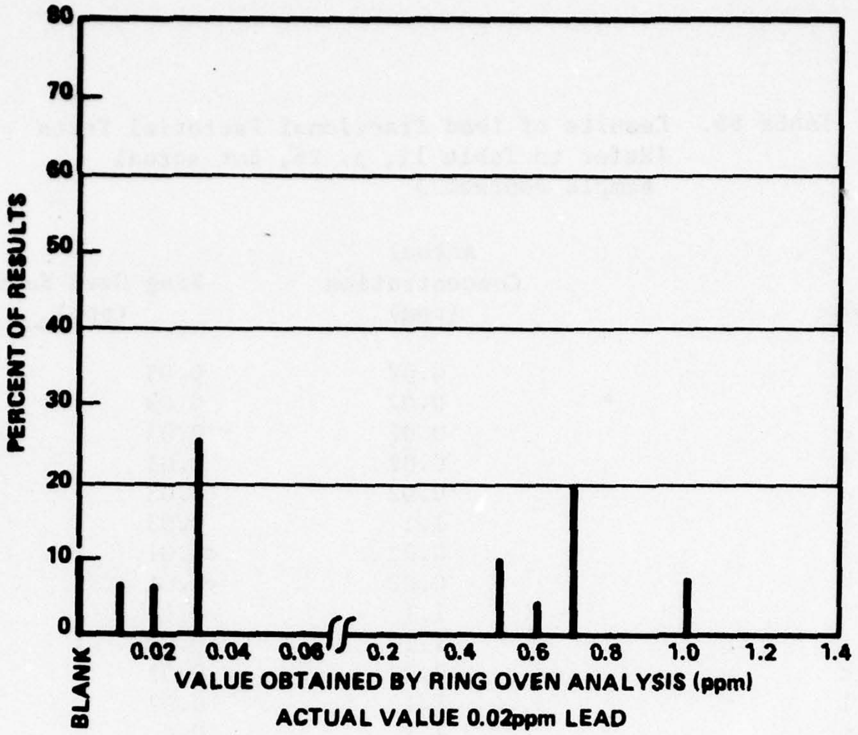
Standards: 0.01 - 0.05 - 1

*Numbers in parentheses represent repeat analysis.

TABLE 66. Results of Lead Fractional Factorial Tests (Refer to Table 11, p. 26, for actual sample content.)

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 0.02 | 0.03 | 0.7 |
| b | 0.02 | 0.03 | 0.7 |
| c | 0.02 | 0.03 | 0.03 |
| d | 0.02 | 0.03 | 0.3 |
| e | 0.02 | 0.03 | 0.7 |
| f | 1.1 | 0.03 | 0.7 |
| g | 0.02 | <0.01 | 0.7 |
| h | 0.02 | <0.01 | 0.5 |
| i | 1.1 | 0.03 | 0.7 |
| j | 1.1 | 0.03 | 0.7 |
| k | 0.02 | 0.02 | 0.03 |
| l | 1.1 | 0.02 | 0.03 |
| m | 1.1 | 0.6 | 0.7 |
| n | 0.02 | 0.7 | 1.0 |
| o | 0.02 | 0.3 | 0.3 |
| p | 1.1 | 0.01 | 1.0 |
| q | 0.02 | 0.5 | 1.0 |
| r | 1.1 | <0.01 | 0.01 |
| s | 1.1 | 0.01 | 0.02 |
| t | 1.1 | 0.3 | >1.0 |
| u | 0.02 | 0.03 | 0.6 |
| v | 0.02 | <0.01 | 0.7 |
| w | 1.1 | 0.01 | >1.0 |
| x | 0.02 | 0.3 | 0.5 |
| y | 1.1 | 0.3 | >1.0 |
| z | 0.02 | 0.01 | 0.3 |
| aa | 1.1 | >1.0 | >1.0 |
| bb | 0.02 | 0.01 | 0.3 |
| cc | 1.1 | 0.01 | >1.0 |
| dd | 1.1 | 0.3 | 1.0 |
| ee | 1.1 | 0.03 | 0.5 |
| ff | 1.1 | 0.5 | 0.7 |

Standards: 0.01 - 0.05 - 1
Operator #4



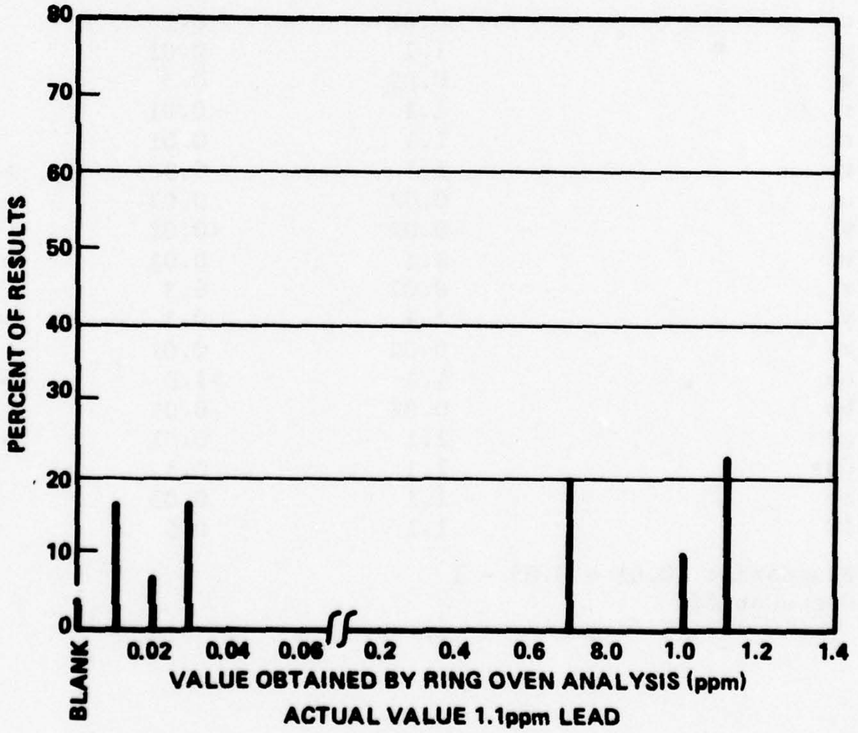


Figure 15. Percent Distribution of Lead Fractional Factorial Test Results at Tested Ion Concentrations

TABLE 67(a). Statistical Analysis of Lead Fractional Factorial Tests

$S_p^2/2$ used for residual mean square

**Analysis of Variance**

| All Observations | | | High Ion Concentration | | | Low Ion Concentration | | |
|---|---|---|---|---|---|---|---|---|
| **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** |
| 1 | 0.02 | 0.22 | 1 | 0.08 | 0.71 | 1 | 0.01 | 0.13 |
| 2 | 0.04 | 0.54 | 2 | 0.06 | 0.58 | 2 | 0.00 | 0.04 |
| 3 | 0.11 | 1.35 | 3 | 0.28 | 2.67 | 3 | 0.00 | 0.08 |
| 4 | 0.16 | 2.01 | 4 | 0.20 | 1.90 | 4 | 0.01 | 0.27 |
| 5 | 0.21 | 2.60 | 5 | 0.20 | 1.87 | 5 | 0.04 | 0.74 |
| 6 | 7.08 | 88.47** | 12 | 0.11 | 1.08 | 12 | 0.03 | 0.47 |
| 12 | 0.12 | 1.55 | 13 | 0.09 | 0.82 | 13 | 0.05 | 0.83 |
| 13 | 0.00 | 0.04 | 14 | 0.00 | 0.02 | 14 | 0.12 | 2.18 |
| 14 | 0.08 | 0.94 | 15 | 0.04 | 0.36 | 15 | 0.01 | 0.13 |
| 15 | 0.04 | 0.49 | 23 | 0.08 | 0.73 | 23 | 0.04 | 0.80 |
| 16 | 0.06 | 0.81 | 24 | 0.01 | 0.14 | 24 | 0.10 | 1.78 |
| 23 | 0.00 | 0.03 | 25 | 0.07 | 0.65 | 25 | 0.00 | 0.00 |
| 24 | 0.09 | 1.17 | 34 | 0.00 | 0.01 | 34 | 0.21 | 3.85 |
| 25 | 0.03 | 0.39 | 35 | 0.03 | 0.29 | 35 | 0.03 | 0.53 |
| 26 | 0.02 | 0.25 | 45 | 0.05 | 0.45 | 45 | 0.09 | 1.58 |
| 34 | 0.09 | 1.17 | | | | | | |
| 35 | 0.06 | 0.74 | | | | | | |
| 36 | 0.18 | 2.22 | | | | | | |
| 45 | 0.00 | 0.04 | | | | | | |
| 46 | 0.05 | 0.66 | | | | | | |
| 56 | 0.03 | 0.37 | | | | | | |
| $S_p^2 = 0.160$ | | | $S_p^2 = 0.211$ | | | $S_p^2 = 0.109$ | | |

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

**A two digit number represents the interaction between the two factor corresponding to the composite digits; i.e., 24 = color interacting with reagent age.**

*** = significant effect**
**** = highly significant effect**

## TABLE 67(b). Statistical Analysis of Lead Fractional Factorial Tests

### Analysis of Variance - All Observations

Residual Mean Square = 0.06192†

| Factor | SS | F Value |
|---|---|---|
| 1 | 0.02 | 0.29 |
| 2 | 0.04 | 0.70 |
| 3 | 0.11 | 1.75 |
| 4 | 0.16 | 2.60 |
| 5 | 0.21 | 3.36 |
| 6 | 7.08 | 114.38** |
| 12 | 0.12 | 2.01 |
| 13 | 0.00 | 0.05 |
| 14 | 0.08 | 1.22 |
| 15 | 0.04 | 0.63 |
| 16 | 0.06 | 1.05 |
| 23 | 0.00 | 0.04 |
| 24 | 0.09 | 1.51 |
| 25 | 0.03 | 0.50 |
| 26 | 0.02 | 0.32 |
| 34 | 0.09 | 1.51 |
| 35 | 0.06 | 0.96 |
| 36 | 0.18 | 2.87 |
| 45 | 0.00 | 0.05 |
| 46 | 0.05 | 0.86 |
| 56 | 0.03 | 0.48 |

†For this table, the lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

TABLE 67 (c). Statistical Analysis of Lead Fractional Factorial Tests

The Average Errors for the High and Low Levels of Each Factor Are:
(Measured ion level minus actual ion level)

| | High | Low |
|---|---|---|
| 1 | -0.189 | -0.142 |
| 2 | -0.129 | -0.202 |
| 3 | -0.108 | -0.224 |
| 4 | -0.237 | -0.095 |
| 5 | -0.085 | -0.246 |
| 6 | -0.636 | 0.305 |

(All observations)

| | High | Low |
|---|---|---|
| 1 | -0.705 | -0.568 |
| 2 | -0.574 | -0.698 |
| 3 | -0.503 | -0.769 |
| 4 | -0.748 | -0.524 |
| 5 | -0.525 | -0.747 |

(At the high ion concentration)

| | High | Low |
|---|---|---|
| 1 | 0.326 | 0.283 |
| 2 | 0.317 | 0.293 |
| 3 | 0.288 | 0.321 |
| 4 | 0.275 | 0.335 |
| 5 | 0.355 | 0.255 |

(At the low ion concentration)

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

TABLE 68. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Lead

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | - | - | - | - | - | - |
| Color | - | - | - | - | - | - |
| Detection Reagent Temperature | - | - | - | - | - | - |
| Reagent Age | - | - | - | - | - | - |
| Chlorine Concentration | - | - | - | - | - | - |
| Ion Concentration | - | - | - | - | - | ** |

- = no significant effect
* = significant effect
** = highly significant effect

eliminating contamination by interferences can be located, the ring oven test for lead should offer a sensitive technique for the determination of this ion.

### 5.1.7 Chloride

Chloride is determined on the ring oven using the reaction between silver chloride and ultraviolet light. Original standards used were blank, 10, 100, 500, 1,000, 5,000, 10,000, and 20,000 ppm chloride to cover the range from 10 to 20,000 ppm chloride.

#### Procedure Adjustment

In order to sharpen the rings and increase ring intensity gradation, a variation in the procedure was developed. The sample was washed to the 22 mm ring with $H_2O$, then the $AgNO_3$ was also washed to the 22 mm ring. Thus, all insoluble silver salts are precipitated at the ring zone. Dilute $HNO_3$ was then applied in order to dissolve most of the silver salts, leaving the silver chloride deposited in the ring. Bromides, iodides, and sulfides should also be deposited; however, their concentrations should be negligible in most natural waters. This procedure, which is given in Appendix C, was used during the statistical evaluations.

#### Operator Variability Tests

There are several chloride decision levels: 15, 250, 600, and 1500 ppm chloride. The first three were considered in one standard range of blank, 15, 250, 600 and 1250 ppm. Ten synthetic water samples were then analyzed using these standard values. The results of this analysis are presented in Table 69. As can be observed from this data, results were somewhat erratic. It was decided to drop the 1250 ppm standard, and change from 600 to 700 ppm standards. Ten samples were then analyzed, with the results obtained given in Table 70.

The standards (blank, 15, 250, and 700 ppm) were then submitted to the Army for approval. The Army requested that Atlantic Research drop the 15 ppm and 250 ppm decision levels, and concentrate on the 600 ppm level. Complying with this request, 200, 400, 600 and 1,000 ppm chloride were chosen for use as permanent standards and in statistical evaluation.

TABLE 69. Operator Variability Tests - Chloride, Run No. 1

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| A | 250 | 250 | 50 |
| B | 1250 | 500 | 600 |
| C | 600 | 600 | 250 |
| D | 15 | Blank | Blank |
| E | 15 | 15 | Blank |
| F | 600 | 250 | 150 |
| G | Blank | 250 | Blank |
| H | Blank | 200 | Blank |
| I | 1250 | 1250 | 1250 |
| J | 250 | 200 | 500 |

15 µl samples
Standards: Blank - 15 - 250 - 600 - 1250
Decision Level: 15 - 250 - 600 - 1500 ppm

---

Table 70. Operator Variability Tests - Chloride, Run No. 2

| Sample | Actual Concentration (ppm) | Ring Oven Restults Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| N | 700 | 300(700)* | 500(700) |
| M | 250 | 250 | 250 |
| L | 250 | 250 | 250 |
| J | 250 | 300 | 250 |
| D | 15 | 15 | Blank |
| G | Blank | 250 | Blank |
| A | 250 | 650 | 300 |
| H | Blank | Blank | Blank |
| E | 15 | 15 | Blank |
| K | 700 | 700 | 700 |

15 µl samples
Standards: Blank - 15 - 250 - 700
Decision Level: 15 - 205 - 600 - 1500 ppm

*Number in parentheses represents repeat analysis.

## Fractional Factorial Tests

Table 71 presents the results of the fractional factorial testing for the chloride ion while Figure 16 graphically presents the results of these tests. Tables 72(a), (b) and (c) present the statistical evaluation of the results of this testing. For all observations, only ion concentration and the interaction of reagent age and chlorine concentration had a highly significant effect (indicated by a double star). Many of the low results obtained at the 1100 ppm $Cl^-$ concentration were from samples containing a high free chlorine level. The effect of free chlorine concentration is apparently not due to the presence of $Cl^-$ in the standard chlorine solution, as the effect due to chlorine concentration for the low ion concentration is not at all significant. The free chlorine effects, however, may be the result of hypochlorous acid (HOCl) with some species in the water sample. Table 73 summarizes the results of the fractional factorial tests for chloride.

## Qualifications Tests

The data obtained from the qualifications tests for the chloride ion are given in Table 74. Table 75 shows the results for the blank tests for this ion. Statistical analysis of the qualifications tests are presented in Table 76. Figure 17 shows the permanent standard rings used in qualifications testing.

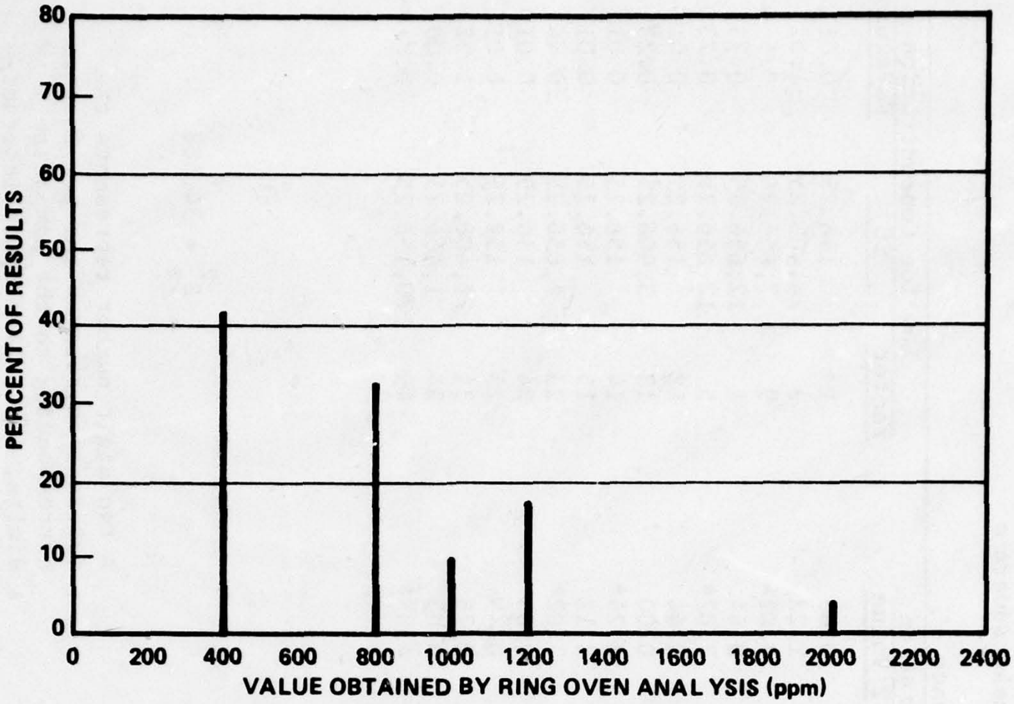
For this ion, the standards were 200, 400, 600 and 1000 ppm. The ion concentrations used were 300, 500, 700 and 1,100 ppm. For this ion, the data are not too consistent. At the higher ion concentrations, the measurements are consistently high (though not too high). This is easily seen in the tables giving the average errors of measurement. When one considers, however, the broad range covered by the four samples, and the greater difficulty one encounters in differentiating between dark-hued rings, the errors are probably not excessive.

From the analysis of variance table, we find highly significant effects due to operator, ion concentration and their interaction. The value for precision, $S_p^2$, is again somewhat smaller than that obtained in the

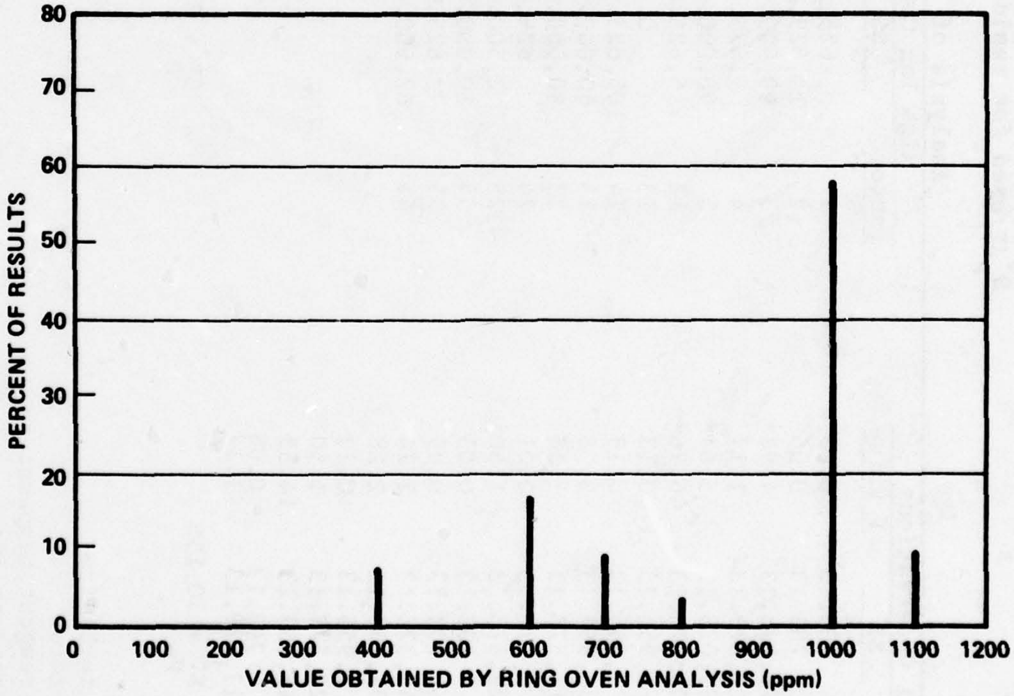
TABLE 71. Results of Chloride Fractional Factorial Tests (Refer to Table 11, p. 26, for actual sample content.)

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 300 | 600 | 600 |
| b | 300 | 400 | 600 |
| c | 300 | 200 | 1000 |
| d | 300 | 400 | 500 |
| e | 300 | 400 | 200 |
| f | 1100 | 1000 | 1000 |
| g | 300 | 200 | 200 |
| h | 300 | 200 | 200 |
| i | 1100 | 600 | 400 |
| j | 1100 | 1000 | 800 |
| k | 300 | 400 | 400 |
| l | 1100 | 700 | 600 |
| m | 1100 | 1000 | 1000 |
| n | 300 | 200 | 400 |
| o | 300 | 400 | 200 |
| p | 1100 | 1000 | 1000 |
| q | 300 | 600 | 500 |
| r | 1100 | 1000 | 1000 |
| s | 1100 | 700 | 1000 |
| t | 1100 | 600 | 600 |
| u | 300 | 400 | 400 |
| v | 300 | 200 | 400 |
| w | 1100 | 1000 | >1000 |
| x | 300 | 200 | 200 |
| y | 1100 | 1000 | 1000 |
| z | 300 | 200 | 600 |
| aa | 1100 | >1000 | 1000 |
| bb | 300 | 500 | 200 |
| cc | 1100 | >1000 | 1000 |
| dd | 1100 | 1000 | 600 |
| ee | 1100 | 400 | 1000 |
| ff | 1100 | 1000 | 700 |

Standards: 200 - 400 - 600 - 1000
Operator #4



ACTUAL VALUE 300ppm CHLORIDE



ACTUAL VALUE 1100ppm CHLORIDE

Figure 16. Percent Distribution of Chloride Fractional Factorial Test Results at Tested Ion Concentrations

TABLE 72(a). Statistical Analysis of Chloride Fractional Factorial Tests

$S_p^2/2$ used for residual mean square

| Analysis of Variance | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| All Observations | | | High Ion Concentration | | | Low Ion Concentration | | |
| Factor | SS | F Value | Factor | SS | F Value | Factor | SS | F Value |
| 1 | 703.13 | 0.05 | 1 | 625.00 | 0.05 | 1 | 156.25 | 0.01 |
| 2 | 703.13 | 0.05 | 2 | 15,625.00 | 1.22 | 2 | 26,406.25 | 1.52 |
| 3 | 75,078.13 | 4.98* | 3 | 90,000.00 | 7.02* | 3 | 7,656.25 | 0.44 |
| 4 | 17,578.13 | 1.17 | 4 | 5,625.00 | 0.44 | 4 | 12,656.25 | 0.73 |
| 5 | 85,078.13 | 5.64* | 5 | 90,000.00 | 7.02* | 5 | 12,656.25 | 0.73 |
| 6 | 705,078.13 | 46.76** | 12 | 5,625.00 | 0.44 | 12 | 156.25 | 0.01 |
| 12 | 1,953.13 | 0.13 | 13 | 0.00 | 0.00 | 13 | 3,906.25 | 0.23 |
| 13 | 1,953.13 | 0.13 | 14 | 105,625.00 | 8.24* | 14 | 156.25 | 0.01 |
| 14 | 56,953.13 | 3.78 | 15 | 40,000.00 | 3.12 | 15 | 156.25 | 0.01 |
| 15 | 17,578.13 | 1.17 | 23 | 90,000.00 | 7.02* | 23 | 7,656.25 | 0.44 |
| 16 | 78.13 | 0.01 | 24 | 625.00 | 0.05 | 24 | 156.25 | 0.01 |
| 23 | 22,578.13 | 1.50 | 25 | 2,500.00 | 0.20 | 25 | 156.25 | 0.01 |
| 24 | 703.13 | 0.05 | 34 | 10,000.00 | 0.78 | 34 | 26,406.25 | 1.52 |
| 25 | 703.13 | 0.05 | 35 | 625.00 | 0.05 | 35 | 1,406.25 | 0.08 |
| 26 | 41,328.13 | 2.74 | 45 | 62,500.00 | 4.88* | 45 | 170,156.25 | 9.81** |
| 34 | 34,453.13 | 2.28 | | | | | | |
| 35 | 1,953.13 | 0.13 | | | | | | |
| 36 | 22,578.13 | 1.50 | | | | | | |
| 45 | 219,453.13 | 14.55 | | | | | | |
| 46 | 703.13 | 0.05 | | | | | | |
| 56 | 17,578.13 | 1.17 | | | | | | |
| | $S_p^2 = 30,156$ | | | $S_p^2 = 25,625$ | | | $S_p^2 = 34,688$ | |

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 72(b). Statistical Analysis of Chloride Fractional Factorial Tests

### Analysis of Variance - All Observations

Residual Mean Square = 16,953†

| Factor | SS | F Value |
|---|---|---|
| 1 | 703.13 | 0.04 |
| 2 | 703.13 | 0.04 |
| 3 | 75,078.13 | 4.43 |
| 4 | 17,578.13 | 1.04 |
| 5 | 85,078.13 | 5.02 |
| 6 | 705,078.13 | 41.59** |
| 12 | 1,953.13 | 0.12 |
| 13 | 1,953.13 | 0.12 |
| 14 | 56,953.13 | 3.36 |
| 15 | 17,578.13 | 1.04 |
| 16 | 78.13 | 0.00 |
| 23 | 22,578.13 | 1.33 |
| 24 | 703.13 | 0.04 |
| 25 | 703.13 | 0.04 |
| 26 | 41,328.13 | 2.44 |
| 34 | 34,453.13 | 2.03 |
| 35 | 1,953.13 | 0.12 |
| 36 | 22,578.13 | 1.33 |
| 45 | 219,453.13 | 12.94** |
| 46 | 703.13 | 0.04 |
| 56 | 17,578.13 | 1.04 |

†For this table, the lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 72(c). Statistical Analysis of Chloride Fractional Factorial Tests

The Average Errors for the High and Low Levels of Each Factor Are:
(Measured ion level minus actual ion level)

|  | High | Low |
|---|---|---|
| 1 | -75.000 | -65.625 |
| 2 | -75.000 | -65.625 |
| 3 | -21.875 | -118.750 |
| 4 | -93.750 | -46.875 |
| 5 | -121.875 | -18.750 |
| 6 | -218.750 | 78.125 |

(For all observations)

|  | High | Low |
|---|---|---|
| 1 | -225.000 | -212.500 |
| 2 | -187.500 | -250.000 |
| 3 | -143.750 | -293.750 |
| 4 | -237.500 | -200.000 |
| 5 | -293.750 | -143.750 |

(At the high ion concentration)

|  | High | Low |
|---|---|---|
| 1 | 75.000 | 81.250 |
| 2 | 37.500 | 118.750 |
| 3 | 100.000 | 56.250 |
| 4 | 50.000 | 106.250 |
| 5 | 50.000 | 106.250 |

(At the low ion concentration)

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

TABLE 73. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Chloride

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | - | - | - | - | - | - |
| Color | - | - | - | - | - | - |
| Detection Reagent Temperature | - | - | * | - | - | - |
| Reagent Age | - | - | - | - | - | - |
| Chlorine Concentration | - | - | - | - | * | - |
| Ion Concentration | - | - | - | - | - | ** |

- = no significant effect
* = significant effect
** = highly significant effect

### Table 74. Chloride Qualifications Tests

Standards: 200 - 400 - 600 - 1000

| | | | | Ion Concentration | | |
|---|---|---|---|---|---|---|
| **Water Sample** | **Operator** | **Measurement** | **300 ppm** | **500 ppm** | **700 ppm** | **1000 ppm** |
| **Turbid** | 1 | 1 | 400 | 500 | 700 | 700 |
| | | 2 | 450 | 750 | 700 | 900 |
| | 2 | 1 | 250 | 375 | 600 | 950 |
| | | 2 | 300 | 425 | 400 | 700 |
| | 3 | 1 | 500 | 400 | 425 | 550 |
| | | 2 | 500 | 400 | 550 | 500 |
| **High TDS** | 1 | 1 | 400 | 850 | 650 | 950 |
| | | 2 | 400 | 375 | 550 | 900 |
| | 2 | 1 | 325 | 400 | 575 | 900 |
| | | 2 | 410 | 450 | 450 | 800 |
| | 3 | 1 | 350 | 400 | 450 | 590 |
| | | 2 | 400 | 390 | 600 | 550 |
| **Colored** | 1 | 1 | 400 | 350 | 450 | 800 |
| | | 2 | 550 | 800 | 550 | 950 |
| | 2 | 1 | 350 | 500 | 600 | 900 |
| | | 2 | 350 | 300 | 300 | 1,000 |
| | 3 | 1 | 400 | 400 | 400 | 500 |
| | | 2 | 390 | 575 | 550 | 600 |
| **Well** | 1 | 1 | 400 | 400 | 500 | 1,000 |
| | | 2 | 400 | 500 | 650 | 750 |
| | 2 | 1 | 350 | 500 | 600 | 900 |
| | | 2 | 350 | 300 | 300 | 1,000 |
| | 3 | 1 | 350 | 425 | 400 | 400 |
| | | 2 | 225 | 700 | 400 | 900 |
| **Organically Polluted** | 1 | 1 | 400 | 400 | 600 | 800 |
| | | 2 | 550 | 750 | 500 | 700 |
| | 2 | 1 | 350 | 500 | 620 | 800 |
| | | 2 | 300 | 425 | 900 | 800 |
| | 3 | 1 | 400 | 400 | 550 | 600 |
| | | 2 | 350 | 450 | 500 | 400 |

Table 75. Chloride - Blank Tests (ppm)
(All samples consisted of deionized water)

| Operator 1 | Operator 2 | Operator 3 |
|---|---|---|
| 50 | Blank | 150 |
| 100 | 25 | 150 |
| 100 | 10 | 100 |
| 100 | 25 | 90 |
| 50 | Blank | 90 |
| 40 | 50 | 80 |
| 100 | 100 | 100 |
| 75 | 150 | 150 |
| 50 | 50 | 100 |
| 100 | Blank | 90 |
| 125 | 10 | 180 |
| 50 | 5 | 150 |
| 100 | 10 | 550 |
| 50 | 10 | 175 |
| 30 | 15 | 150 |

## TABLE 76. Analysis of Qualifications Tests - Chloride Ion (Refer to Section 4.4 for explanation of terms)

### Analysis of Variance - All Ion Concentrations

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 378,830.417 | 2 | 189,415.208 | 12,176** |
| Ion Level | 3,067,615.833 | 3 | 1,022,538.611 | 13.450** |
| Water Sample | 4,150.000 | 4 | 1,037.500 | 0.155 |
| OPXIONLEV | 456,137.917 | 6 | 76,022.986 | 4.887** |
| OPXWATSAM | 53,686.250 | 8 | 6,710.781 | 0.431 |
| WATSMXIONL | 175,346.667 | 12 | 14,612.222 | 0.939 |
| Precision | 933,400.000 | 60 | 15,556.667 | |

$S_p^2$ = 15,557

$S_o^2$ = 4,346

Third order Interaction MS = 9,286

### Average Errors of Measurement

(Measured Ion Concentration Minus Actual Ion Concentration)

| | Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| **Operator** | 300 | 500 | 700 | 1100 |
| 1 | 135.00 | 67.50 | -115.00 | -255.00 |
| 2 | 33.50 | -82.50 | -165.50 | -225.00 |
| 3 | 86.50 | -46.00 | -217.50 | -541.00 |
| **Water Sample** | | | | |
| Turbid | 100.00 | -25.00 | -137.50 | -383.33 |
| High TDS | 80.83 | -22.50 | -154.17 | -318.33 |
| Colored | 106.67 | -12.50 | -225.00 | -308.33 |
| Well | 45.83 | -29.17 | -225.00 | -275.00 |
| Organically Polluted | 91.67 | -12.50 | -88.33 | -416.67 |

| | Operator | | |
|---|---|---|---|
| **Water Sample** | 1 | 2 | 3 |
| Turbid | -12.50 | -150.00 | -171.88 |
| High TDS | -15.63 | -111.25 | -183.75 |
| Colored | -43.75 | -112.50 | -173.13 |
| Well | -75.00 | -112.50 | -175.00 |
| Organically Polluted | -62.50 | -63.13 | -193.75 |

## TABLE 76. (Continued)

## Analysis of Variance for Each Ion Concentration

The ion concentration is 300 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 51,545.000 | 2 | 25,772.500 | 9.611** |
| Water Sample | 13,741.667 | 4 | 3,435.417 | 0.507 |
| OPXWATSAM | 54,188.333 | 8 | 6,773.542 | 2.526 |
| Precision | 40,225.000 | 15 | 2,681.667 | |

$S_p^2 = 2,682$

$S_p^o = 557$

$\overline{X} = 385$

The ion concentration is 500 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 122,381.667 | 2 | 61,190.833 | 2.232 |
| Water Sample | 1,363.333 | 4 | 340.833 | 0.033 |
| OPXWATSAM | 83,401.667 | 8 | 10,425.208 | 0.380 |
| Precision | 411,300.000 | 15 | 27,420.000 | |

$S_p^2 = 27,420$

$S_o^2 = 0$(1)

$\overline{X} = 479.667$

The ion concentration is 700 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 52,535.000 | 2 | 26,267.500 | 1.834 |
| Water Sample | 83,678.333 | 4 | 20,919.583 | 1.456 |
| OPXWATSAM | 114,931.667 | 8 | 14,366.458 | 1.003 |
| Precision | 214,825.000 | 15 | 14,321.667 | |

$S_p^2 = 14,321$

$S_2^o = 0$(1)

$\overline{X} = 533.000$

The ion concentration is 1100 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 608,506.667 | 2 | 304,253.333 | 17.090** |
| Water Sample | 80,713.333 | 4 | 20,178.333 | 6.719* |
| OPXWATSAM | 24,026.667 | 8 | 3,003.333 | 0.169 |
| Precision | 267,050.000 | 15 | 17,803.333 | |

$S_p^2 = 17,803$

$S_o^2 = 28,645$

$\overline{X} = 759.667$

(1) If the F value for Operator effect is not significant, $S_o^2$ is considered to be zero.

TABLE 76. (Continued)

## Average Errors for Individual Factors

| Operator | Average Error |
|---|---|
| 1 | -41.875 |
| 2 | -109.875 |
| 3 | -179.500 |
| **Water Sample** | |
| Turbid | -111.458 |
| High TDS | -103.542 |
| Colored | -109.792 |
| Well | -120.833 |
| Organically Polluted | -106.458 |
| **Ion Concentration** | |
| 300 ppm | 85.000 |
| 500 ppm | -20.333 |
| 700 ppm | -166.000 |
| 1100 ppm | -340.333 |

Figure 17. Chloride Rings

fractional factorial test. The estimate of operator variability is again considerably smaller than $S_p^2$. Table 75 shows no false positives exceeding the lower water level tested; however, the background levels of chloride in filter papers, reagents, etc., resulted in some ring color in almost every case.

Referring to the method suggested in Section 4.4.4 (p. 38) for use of the ring oven technique as a screening procedure, we see that it would not perform quite as well in the case of this ion as for the ones considered in the previous sections. The distribution of results at each ion concentration for the 15 pairs of measurements are given in Table 77. From these results, it is evident that when the actual ion concentration is below the critical level of 600 ppm, the screening procedure works quite well. When the ion concentration is above 600 ppm, however, this is not the case, particularly when the concentration is only slightly above the critical level. Note that these conclusions are rather tentative as discussed in Section 4.4.4. Figure 18 gives a graphic representation of the general screening analysis. As can be seen from the bar graph at the 1100 ppm level, 77% of the "go-no go" decisions were made correctly.

## Conclusions

The reason for the inconsistent results for the chloride tests is, in all probability, due to standard ring values that are too close together. It must be remembered that the rings obtained for chloride are brown-black in color and thus they are harder to differentiate between than rings of a lighter, brighter hue. In the previous contractual effort, the minimum ring gradation used around the decision area of 600 ppm was a 500 ppm increment. During this year's effort, this was changed to a 200 to 400 ppm increment. It would appear that this step is not sufficient to give reliable differentiation.

The chloride test, however, should still be suitable for use as a screening method in determining water potability with an adjustment to broaden standard values. Even at the present standard values, the extremes of the samples tested were placed on the correct side of the

TABLE 77. Distribution of Replicate Results Around Decision Level for Chloride Qualifications Tests

Decision Concentration - 600 ppm

| Ring Oven Results | Sample Ion Concentration (ppm)<br>300 | 500 | 700 | 1100 |
|---|---|---|---|---|
| Both $\geq$ 600 (1) | 0 | 0 | 2 | 10 |
| Both < 600 (2) | 15 | 10 | 6 | 2 |
| Other (3) | 0 | 5 | 7 | 3 |

(1) The ion concentration is deemed unacceptable.

(2) The ion concentration is deemed acceptable.

(3) More measurement is required before a decision can be made.

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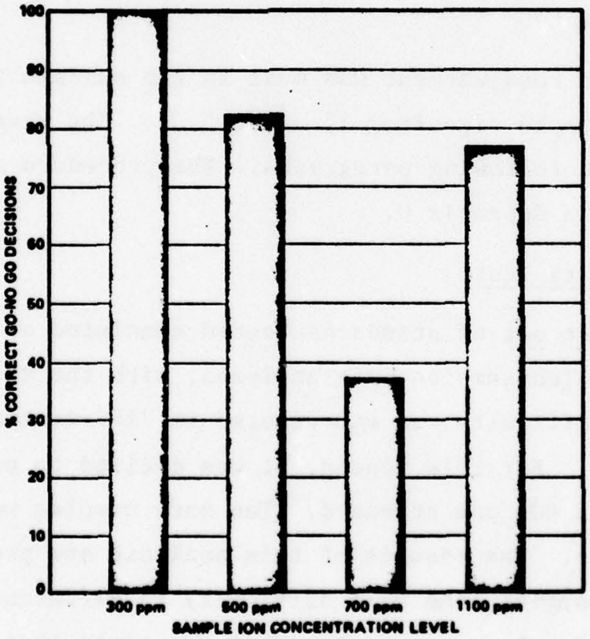


Figure 18. Percent Correct "Go-No Go" Decisions for Chloride (Based on a decision concentration of 600 ppm)

decision level 77% of the time; in only two out of thirty cases were both measurements of a single sample on the wrong side of the decision level at the extreme sample concentrations. The only highly significant effect found for this ion, ion concentration, should be corrected by broadening the standard increments.

### 5.1.8 Sulfate

The reaction of barium sulfate with rhodizonate was chosen for the ring oven determination of the sulfate anion. While many anions will form insoluble barium salts that can react with rhodizonate in addition to sulfate, most are eliminated in the ring oven procedure by the use of an acid wash solution, except for sulfate. See reference (1) for a further discussion of barium-rhodizonate's reactivity.

The range for which this reagent was evalauted was from 10 to 3,000 ppm sulfate, with standards of 10, 100, 500, 1,000, 2,000, and 3,000 ppm.

#### Procedure Adjustment

No major readjustment was made in the sulfate procedure, except for a change in sample size from 15 μl to 5 μl. The reason for this change is dicussed in the following paragraphs. The procedure used for statistical testing is given in Appendix C.

#### Operator Variability Tests

The first set of standards tested consisted of 50, 250, 600 and 1,000 ppm rings. Ten samples were analyzed, with the results given in Table 78. Some difficulty was encountered in differentiating between 600 and 1000 ppm $SO_4^=$. For this reason, it was decided to use a 500 ppm standard rather than a 600 ppm standard. Ten more samples were analyzed with a new standard set. The results of this analysis are presented in Table 79. As can be observed, the same difficulty in differentiating between the two upper standard values occurred. This suggested that a smaller sample size might be indicated, in order to bring the ring values down below the upper reagent limit of 15 μg $SO_4^=$.

Twenty samples were then analyzed using 5 μl samples (instead of 15 μl samples) and 50, 250, 600 and 1000 ppm standards. Table 80 gives

## TABLE 78. Operator Variability Tests - Sulfate, Run No. 1

| Sample | Actual $SO_4$ Concentration (ppm) | $SO_4$ Found Operator No. 1 (ppm) | $SO_4$ Found Operator No. 2 (ppm) |
|---|---|---|---|
| A | 600 | 1000 | 1000 |
| B | 1000 | 1000 | 600 |
| C | 50 | 50 | 50 |
| D | 600 | 600 | 250 |
| E | 50 | 50 | 50 |
| F | 1000 | 600 | 1000 |
| G | 250 | 250 | 250 |
| H | 600 | 1000 | 600 |
| I | 1000 | 1000 | 1000 |
| J | 50 | 250 | 50 |

15 µl samples
Standards: 50 - 250 - 600 - 1000
Decision Levels: 250 - 400 - 2700 ppm

---

## TABLE 79. Operator Variability Tests - Sulfate, Run No. 2

| Sample | Actual $SO_4$ Concentration (ppm) | $SO_4$ Found Operator No. 1 (ppm) | $SO_4$ Found Operator No. 2 (ppm) |
|---|---|---|---|
| K | 250 | 500 | 600 |
| L | 1000 | 1000 | 1000 |
| M | 1000 | 1000 | 600 |
| N | 250 | 500 | 1000 |
| O | Blank | Blank | Blank |
| P | 600 | 1000 | 600 |
| Q | 250 | 500 | 1000 |
| R | 50 | 50 | 150 |
| S | 250 | 500 | 600 |
| T | 600 | 1000 | 1000 |
| AA | 500 | 1000 | 1000 |
| BB | 500 | 500 | 500 |
| CC | 500 | 1000 | 500 |

15 µl samples
**Standards:** 50 - 250 - 500 - 1000
**Decision Levels:** 250 - 400 - 2700

## TABLE 80. Operator Variability Tests - Sulfate, Run No. 3

| Sample | Actual $SO_4$ Concentration (ppm) | $SO_4$ Found Operator No. 1 (ppm) | $SO_4$ Found Operator No. 2 (ppm) |
|---|---|---|---|
| A | 600 | 1000 | >1000 |
| B | 1000 | 1000 | - |
| C | 50 | 50 | 50 |
| D | 600 | 1000 | 500 |
| E | 50 | 1000 | 50 |
| F | 1000 | 1000 | 1000 |
| G | 250 | 600 | 250 |
| H | 600 | 1000 | 1000 |
| I | 1000 | 1000 | 500 |
| J | 50 | 50 | 50 |
| K | 250 | 600 | 250 |
| L | 1000 | 1000 | >1000 |
| M | 1000 | 1000 | 400 |
| N | 250 | 250 | 150 |
| O | Blank | Blank | <50 |
| P | 600 | 1000 | 1000 |
| Q | 250 | 250 | 350 |
| R | 50 | 50 | 50 |
| S | 250 | 600 | 350 |
| T | 600 | 250 | 800 |

**5 µl samples**

**Standards: 50 - 250 - 600 - 1000**

**Decision Levels: 250-400-2700 ppm**

*** Operator # 3 had some previous ring oven experience.**

the results of this analysis. While these results are more satisfactory, the differentiation between 600 and 1000 ppm is still not as reliable as desired. In addition, it can be observed from the data in Table 80 that the more experienced ring oven operator (Operator No. 3) shows better results than the inexperienced operator.

It was thought that elimination of the 600 ppm ring and addition of a 3000 ppm ring might solve the problem of reliability in the area of 600 ppm. Thus, more samples were analyzed using 5 µl samples and 50, 250, 1000, and 3000 ppm standards before any decision as to standard levels was made. The results of this analysis are presented in Table 81. More satisfactory results were obtained.

A question also arose as to whether the operators were properly reading the rings. It was frequently observed that only standard values or previous standard values are given for unknown ring concentrations, despite instructions to interpolate between standard values when applicable. This suggested a bias on the part of the operators in the direction of the standards, which appeared to exist regardless of how the standards were labeled. Once the standards were viewed by the operators and a few unknowns compared to them, a tendency to favor the standards existed. This was investigated by having a third party read the $SO_4^=$ rings, and by closer observation of the operators during ring quantitation.

Table 81 gives readings of the $SO_4^=$ sample rings by a third party. In most cases, results were in close agreement, which indicated that no bias existed on the part of the operators. Even if such a bias did exist during initial sample analysis by a new operator, this bias disappeared as the operator realized that he was not in a "competition" to match exactly the standard values.

The standards submitted to the Army for approval were 50, 250, 1000, and 3000, ppm. The Army requested that Atlantic Research substitute 400 ppm as the decision level in place of 250 ppm. Thus, the standard values used in all subsequent analyses were 50, 400, 1000, and 3000 ppm sulfate.

## TABLE 81. Operator Variability Tests - Sulfate, Run No. 4

| Sample | Actual $SO_4^=$ Concentration (ppm) | $SO_4^=$ Found, Operator #3* (ppm) | Third Party Reading Operator #3* (ppm) | $SO_4^=$ Found, Operator #4* (ppm) | Third Party Reading Operator #4 (ppm) |
|---|---|---|---|---|---|
| C | 50 | 50 | 50 | 50 | 50 |
| J | 50 | 50 | 100 | 40 | 50 |
| A | 600 | 500 | 500 | 1000 | 800 |
| AA | 500 | 250 | 200 | 250 | 400 |
| B | 1000 | 1000 | 800 | 1000 | 1000 |
| K | 250 | 200 | 250 | 250 | 600 |
| XX | 250 | 150 | 250 | 300 | 600 |
| EE | 3000 | 1000 | 2000 | 1000 | 1000 |
| GG | 3000 | 1000 | 1000 | 2000 | 1000 |
| S | 250 | 250 | 250 | 250 | 500 |
| P | 600 | 400 | 600 | 900 | 800 |
| I | 1000 | 800 | 600 | 400 | 600 |
| O | Blank | <50 | Blank | Blank | 10 |
| Q | 250 | 259 | 250 | 50 | 50 |
| M | 1000 | 250 | 600 | 900 | 500 |
| FF | 3000 | 2000 | 3000 | 3000 | 2000 |
| L | 1000 | 1000 | 1000 | 1000 | 800 |
| E | 50 | 50 | 50 | 50 | 50 |
| N | 250 | 100 | 200 | 200 | 200 |
| G | 250 | 250 | 200 | 250 | 200 |
| YY | 250 | 250 | 250 | 300 | 250 |
| F | 1000 | 800 | 900 | 1000 | 800 |
| CC | 500 | 400 | 500 | 900 | 500 |

5 µl Samples.

Standards: 50 25-1000-3000

Decision Levels:  250-400-2700 ppm

*Operators No. 3 and 4 had some previous ring oven experience.

## Fractional Factorial Tests

The results for the fractional factorial tests for the sulfate ion are given in Table 82 and illustrated in Figure 19, while Table 83(a), (b) and (c) shows the statistical evaluation of these results. As can be seen from the statistical evaluation in Table 83, only a few variable effects were encountered, none of these being highly significant. Those variables which proved to have a significant effect for all observations (indicated by a single star) were turbidity, and the interaction of turbidity-ion concentration. Some of the high readings at the 1200 ppm level (samples w, t) may be due to high turbidity levels. Suspicious results were checked whenever time allowed. For example, Sample cc, No. 1 (Table 82, p. 170) gave a very low result; this was due to failure to apply sample. For Sample cc, an analysis was run using 1750 ppm as a replacement measurement. This reduced $S_p^2$ to 65,566 for all measurements and to 130,468 for the high ion concentration. This difference was still striking. Table 84 summarizes the results of the fractional factorial tests for all observations for sulfates.

## Qualification Tests

The results of the qualifications tests for sulfates are given in Table 85. The results of the blank tests are given in Table 86. Table 87 gives the statistical evaluation of the qualifications tests. Figure 20 shows the permanent standard rings used during the qualifications testing.

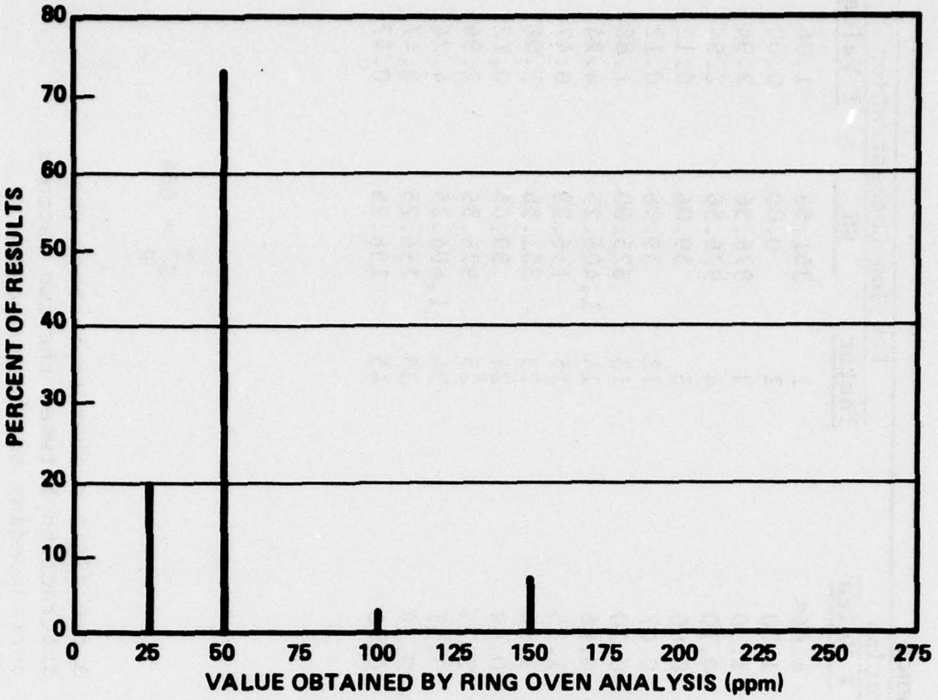
For this ion, the standards were 50, 400, 1000 and 3000 ppm, and the ion concentrations used were 40, 200, 600, and 1200 ppm. Most of the data seems reasonably consistent, although there are a few wide discrepancies between repeated measurements.

From the analysis of variance with all ion concentrations included, we have a highly significant variability due to operators, as well as highly significant interactions between operator and ion concentration and between water sample and ion concentration. This means that different results are obtained at the different ion concentrations, but the changes at the several ion concentrations are different for the different operators and for the different water samples. For instance, from the table giving average errors

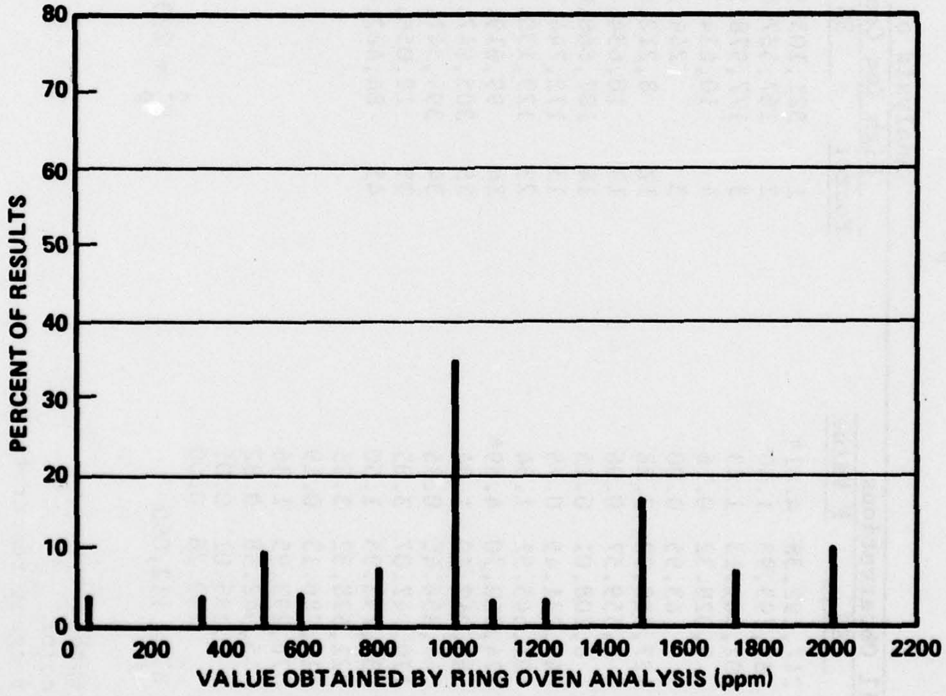
TABLE 82. Results of Sulfate Fractional Factorial Tests (Refer to Table 11, p. 26, for actual sample content.)

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 40 | <50 | 50 |
| b | 40 | 50 | 50 |
| c | 40 | 50 | 50 |
| d | 40 | <50 | 150 |
| e | 40 | <50 | 50 |
| f | 1200 | 1000 | 1000 |
| g | 40 | 50 | 50 |
| h | 40 | 50 | 50 |
| i | 1200 | 500 | 1500 |
| j | 1200 | 350 | 1100 |
| k | 40 | <50 | 50 |
| l | 1200 | 800 | 1000 |
| m | 1200 | 350 | 1000 |
| n | 40 | 50 | 50 |
| o | 40 | 100 | 150 |
| p | 1200 | 500 | 500 |
| q | 40 | 50 | 50 |
| r | 1200 | 1000 | 1000 |
| s | 1200 | 1500 | 1500 |
| t | 1200 | 1250 | 1750 |
| u | 40 | <50 | 50 |
| v | 40 | 50 | 50 |
| w | 1200 | 2000 | 2000 |
| x | 40 | 50 | 50 |
| y | 1200 | 800 | 1500 |
| z | 50 | <50 | 50 |
| aa | 1200 | 1000 | 2000 |
| bb | 40 | 50 | 50 |
| cc | 1200 | <50 | 1750 |
| dd | 1200 | 1000 | 1000 |
| ee | 1200 | 600 | 1000 |
| ff | 1200 | 1000 | 1500 |

Standards: 50 - 400 - 1000 - 2700
Operator No. 6



ACTUAL VALUE 40ppm SULFATE



ACTUAL VALUE 1200ppm SULFATE

Figure 19. Percent Distribution of Sulfate Fractional Factorial Test Results at Tested Ion Concentrations

TABLE 83(a). Statistical Analysis of Sulfate Fractional Factorial Tests

$S_p^2/2$ **used for residual mean square**

| Analysis of Variance | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **All Observations** | | | **High Ion Concentration** | | | **Low Ion Concentration** | | |
| **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** |
| 1 | 247,192.38 | 4.41* | 1 | 521,103.52 | 4.66* | 1 | 351.56 | 1.06 |
| 2 | 83,793,95 | 1.50 | 2 | 167,587.89 | 1.50 | 2 | 0.00 | 0.00 |
| 3 | 102,661.13 | 1.83 | 3 | 177,978.52 | 1.50 | 3 | 976.56 | 2.94 |
| 4 | 9,028.32 | 0.16 | 4 | 10,634.77 | 0.10 | 4 | 976.56 | 2.94 |
| 5 | 43.95 | 0.00 | 5 | 244.14 | 0.00 | 5 | 39.06 | 0.12 |
| 6 | 127,828.32 | 2.28 | 12 | 8,212.89 | 0.07 | 12 | 39.06 | 0.12 |
| 12 | 3,559.57 | 0.06 | 13 | 10,634.77 | 0.10 | 13 | 625.00 | 1.88 |
| 13 | 8,208.01 | 0.15 | 14 | 107,666.02 | 0.96 | 14 | 1,406.25 | 4.24 |
| 14 | 42,231.45 | 0.75 | 15 | 172,744.14 | 1.55 | 15 | 156.25 | 0.47 |
| 15 | 91,645.51 | 1.64 | 23 | 129,150.39 | 1.16 | 23 | 351.56 | 1.06 |
| 16 | 274,262.70 | 4.89* | 24 | 99,619.14 | 0.89 | 24 | 39.06 | 0.12 |
| 23 | 58,012.70 | 1.04 | 25 | 305,947.27 | 2.74 | 25 | 976.56 | 2.94 |
| 24 | 47,856.45 | 0.85 | 34 | 394,541.02 | 3.53 | 34 | 1,406.25 | 4.24 |
| 25 | 170,747.07 | 3.05 | 35 | 18,056.65 | 0.16 | 35 | 156.25 | 0.47 |
| 26 | 83,793.95 | 1.50 | 45 | 84,462.89 | 0.76 | 45 | 156.25 | 0.47 |
| 34 | 221,528.32 | 3.95 | | | | | | |
| 35 | 10,786.13 | 0.19 | | | | | | |
| 36 | 76,293.95 | 1.36 | | | | | | |
| 45 | 45,942.38 | 0.82 | | | | | | |
| 46 | 2,583.01 | 0.05 | | | | | | |
| 56 | 239.26 | 0.00 | | | | | | |
| | $S_p^2 = 112,060$ | | | $S_p^2 = 223,457$ | | | $S_p^2 = 664$ | |

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 83 (b). Statistical Analysis of Sulfate Fractional Factorial Tests

### Analysis of Varience - All Observations

Residual Mean Square = 63,583.01†

| Factor | SS | F Value |
|---|---|---|
| 1 | 247,192.38 | 3.89 |
| 2 | 83,793.95 | 1.32 |
| 3 | 102,661.13 | 1.61 |
| 4 | 9,028.32 | 0.14 |
| 5 | 43,95 | 0.00 |
| 6 | 127,838.32 | 2.01 |
| 12 | 3,559.57 | 0.06 |
| 13 | 8,208.01 | 0.13 |
| 14 | 42,231.45 | 0.66 |
| 15 | 91,645.51 | 1.44 |
| 16 | 274,262.70 | 4.31 |
| 23 | 58,012.70 | 0.91 |
| 24 | 47,856.45 | 0.75 |
| 25 | 170,747.07 | 2.69 |
| 26 | 83,793.95 | 1.32 |
| 34 | 221,528.32 | 3.48 |
| 35 | 10,786.13 | 0.17 |
| 36 | 76,293,95 | 1.20 |
| 45 | 45,942.38 | 0.72 |
| 46 | 2,583.01 | 0.04 |
| 56 | 239.26 | 0.00 |

†For this table, the lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 83(c). Statistical Analysis of Sulfate Fractional Factorial Tests

The Average Errors for the High and Low Levels of Each Factor Are:
(Measured ion level minus actual ion level)

The Average Errors for the High and Low Levels of Each Factor Are:

|  | High | Low |
|---|---|---|
| 1 | 37.813 | -137.969 |
| 2 | 1.094 | -101.250 |
| 3 | 6.563 | -106.719 |
| 4 | -66.875 | -33.281 |
| 5 | -51,250 | -48.906 |
| 6 | -113.281 | 13.125 |

(For all observations)

|  | High | Low |
|---|---|---|
| 1 | 67.188 | -293.750 |
| 2 | -10.938 | -215.625 |
| 3 | -7.813 | -218.750 |
| 4 | -139.063 | -87.500 |
| 5 | -117.188 | -109.375 |

(At the high ion concentration)

|  | High | Low |
|---|---|---|
| 1 | 8.438 | 17.813 |
| 2 | 13.125 | 13.125 |
| 3 | 20.938 | 5.313 |
| 4 | 5.313 | 20.938 |
| 5 | 14.688 | 11.563 |

(At the low ion concentration)

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

TABLE 84. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Sulfate

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | * | - | - | - | - | * |
| Color | - | - | - | - | - | - |
| Detection Reagent Temperature | - | - | - | - | - | - |
| Reagent Age | - | - | - | - | - | - |
| Chlorine Concentration | - | - | - | - | - | - |
| Ion Concentration | * | - | - | - | - | - |

- = no significant effect
* = significant effect
** = highly significant effect

TABLE 85. Sulfate Qualifications Testing
Standards: 50 - 400 - 1000 - 1300

| Water Sample | Operator | Measurement | Ion Concentration<br>40 ppm | <br>200 ppm | <br>600 ppm | <br>1200 ppm |
|---|---|---|---|---|---|---|
| Turbid | 1 | 1 | 100 | 300 | 400 | 1000 |
| | | 2 | 50 | 75 | 400 | 900 |
| | 2 | 1 | 350 | 400 | 1000 | 1100 |
| | | 2 | 300 | 400 | 1000 | 1000 |
| | 3 | 1 | 200 | 300 | 600 | 1000 |
| | | 2 | 200 | 200 | 300 | 1000 |
| High TDS | 1 | 1 | 60 | 200 | 700 | 700 |
| | | 2 | 60 | 200 | 350 | 900 |
| | 2 | 1 | 100 | 300 | 1000 | 1200 |
| | | 2 | 100 | 400 | 1000 | 2000 |
| | 3 | 1 | 200 | 300 | 400 | 900 |
| | | 2 | <50 | 200 | 300 | 1000 |
| Colored | 1 | 1 | 60 | 400 | 200 | 1500 |
| | | 2 | 125 | 75 | 400 | 700 |
| | 2 | 1 | 100 | 100 | 300 | 2600 |
| | | 2 | 100 | 300 | 1000 | 2700 |
| | 3 | 1 | 50 | 100 | 400 | 1000 |
| | | 2 | 50 | 300 | 200 | 1000 |
| Well | 1 | 1 | 50 | 100 | 600 | 700 |
| | | 2 | 60 | 300 | 400 | 500 |
| | 2 | 1 | 50 | 100 | 400 | 400 |
| | | 2 | 60 | 200 | 1000 | 1000 |
| | 3 | 1 | 50 | 300 | 400 | 600 |
| | | 2 | 50 | 200 | 400 | 1000 |
| Organically Polluted | 1 | 1 | 50 | 400 | 100 | 500 |
| | | 2 | 50 | 100 | 300 | 900 |
| | 2 | 1 | 100 | 400 | 100 | 2200 |
| | | 2 | <50 | 150 | 400 | 1000 |
| | 3 | 1 | 50 | 300 | 300 | 1000 |
| | | 2 | 50 | 150 | 300 | 800 |

TABLE 86. Sulfate - Blank Tests (ppm)

All Samples Consisted of Deionized Water

| Operator 1 | Operator 2 | Operator 3 |
|---|---|---|
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | 50 | < 50 |
| < 50 | < 50 | < 50 |
| < 50 | < 50 | < 50 |

## TABLE 87. Analysis of Qualifications Tests - Sulfate Ion (Refer to Section 4.4 for explanation of terms)

### Analysis of Variance - All Ion Concentrations

| Source | S S | DF | MS | F |
|---|---|---|---|---|
| Operator | 1,985,771.667 | 2 | 992,885.833 | 21.945** |
| Ion Level | 751,515.625 | 3 | 250,505.208 | 0.916 |
| Water Sample | 719,506.250 | 4 | 179,876.563 | 2.304 |
| OPXIONLEV | 1,641,115.000 | 6 | 273,519.167 | 6.045** |
| OPXWATSAM | 624,538.750 | 8 | 78,067.344 | 1.725 |
| WATSMXIONL | 2,419,810.417 | 12 | 201,650.868 | 4.457** |
| Precision | 2,714,712.500 | 60 | 45,245.208 | |

$s_p^2$ = 45,245

$s_o^2$ = 23,691

Third Order Interaction MS = 89,798

### Average Errors of Measurement

(Measured Ion Concentration Minus Actual Ion Concentration)

| | Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| **Operator** | 40 | 200 | 600 | 1200 |
| 1 | 26.50 | 15.00 | -215.00 | -370.00 |
| 2 | 88.50 | 75.00 | 120.00 | 320.00 |
| 3 | 52.50 | 35.00 | -240.00 | -270.00 |
| **Water Sample** | | | | |
| Turbid | 160.00 | 79.17 | 16.67 | -200.00 |
| High TDS | 50.83 | 66.67 | 25.00 | -83.33 |
| Colored | 40.83 | 12.50 | -183.33 | 383.33 |
| Well | 13.33 | 00.00 | -66.67 | -500.00 |
| Organically Polluted | 14.17 | 50.00 | -350.00 | -133.33 |

| | Operator | | |
|---|---|---|---|
| **Water Sample** | 1 | 2 | 3 |
| Turbid | -106.88 | 183.75 | -35.00 |
| High TDS | -113.75 | 252.50 | -94.38 |
| Colored | -77.50 | 390.00 | -122.50 |
| Well | -171.25 | -108.75 | -135.00 |
| Organically Polluted | -210.00 | 36.08 | -141.25 |

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## Table 87. (Continued)

## Analysis of Variance for Each Ion Concentration

The ion concentration is 40 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 19,386.667 | 2 | 9,693.333 | 6.367** |
| Water Sample | 87,858.333 | 4 | 21,964.583 | 3.566 |
| OPXWATSAM | 49,271.667 | 8 | 6,158.958 | 4.045* |
| Precision | 22,837.500 | 15 | 1,522.500 | |

$S_p^2 = 1{,}522$

$S_o^2 = 817$

$\underline{\overline{X}} = 95.833$

The ion concentration is 200 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 18,666.667 | 2 | 9,333.333 | 0.559 |
| Water Sample | 28,125.000 | 4 | 7,031.250 | 0.843 |
| OPXWATSAM | 66,750.000 | 8 | 8,343.750 | 0.499 |
| Precision | 250,625.000 | 15 | 16,708.333 | |

$S_p^2 = 16{,}708$

$S_o^2 = 0^{(1)}$

$\underline{\overline{X}} = 241.667$

The ion concentration is 600 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 808,166.667 | 2 | 404,083.333 | 9.166** |
| Water Sample | 594,666.667 | 4 | 148,666.667 | 3.357 |
| OPXWATSAM | 354,333.333 | 8 | 44,291.667 | 1.005 |
| Precision | 661,250.000 | 15 | 44,083.333 | |

$S_p^2 = 44{,}083$

$S_o^2 = 36{,}000$

$\underline{\overline{X}} = 488.333$

The ion concentration is 1200 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 2,780,666.667 | 2 | 1,390,333.333 | 11.716* |
| Water Sample | 2,428,666.667 | 4 | 607,166.667 | 2.103 |
| OPXWATSAM | 2,309,333.333 | 8 | 288,666.667 | 2.433 |
| Precision | 1,780,000.000 | 15 | 118,666.667 | |

$S_p^2 = 118{,}667$

$S_o^2 = 127{,}167$

$\underline{\overline{X}} = 1{,}093.333$

(1) If the F value for operator effect is not significant, $S_o^2$ is considered to be zero.

## TABLE 87. (Continued)

### Average Errors for Individual Factors

| Operator | Average Error |
|---|---|
| 1 | -135.875 |
| 2 | 150.875 |
| 3 | -105.625 |
| **Water Sample** | |
| Turbid | 13.958 |
| High TDS | 14.792 |
| Colored | 63.333 |
| Well | -138.333 |
| Organically Polluted | -104.792 |
| **Ion Concentration** | |
| 40 ppm | 55.833 |
| 200 ppm | 41.667 |
| 600 ppm | -111.667 |
| 1200 ppm | -106.667 |

Figure 20. Sulfate Rings

for the different operators at the different ion concentrations, we see that Operators 1 and 3, on the average, measured considerably below the actual level at the high ion concentrations, but that Operator 2 measured, on the average, considerably above. The average errors for the individual ion concentrations for this test are excellent, considering the broad range covered by the standards and the difficulty in differentiating between dark rings, as described above for the chloride test.

The operator variability (measured by $S_o^2$) is fairly large compared with the precision (measured by $S_p^2$). At the different ion concentrations, we find, again, a significant operator effect. The values for $S_p^2$ measured at the high (1200) and low (40) ion concentrations are reasonably consistent with those obtained for the same ion concentrations in the fractional factorial tests. The blank tests shown in Table 86 gave only two insignificant false positives, both equal to the lowest permanent standard value. This is equivalent to a false positive only 4% of the time.

At each ion concentration, fifteen pairs of measurements were made. The distribution of these measurements around the decision concentration are shown in Table 88. Referring to the method suggested in Section 4.4.4 (p. 38), for using the ring oven for screening purposes, we see that it would appear to work fairly well for this case. When the ion concentration is 40 ppm or 1200 ppm, it appears that this will be determined correctly from initial measurements. When the ion concentration is 200 ppm, the ring oven places the samples on the correct side of the decision concentration in most cases, but when the ion concentration level is above the decision concentration, but close to this value (600 ppm to 400 ppm), two mistakes are made. For this reason, additional measurements would be required. Figure 21 illustrates graphically the results of the general scan analysis. At the extreme water test concentration above the decision level, 30 out of 30 (individual samples) gave correct "go-no go" decisions.

## Conclusions

The ring oven method for the sulfate ion appears to be an efficient technique for screening natural waters for this ion. No highly

TABLE 88. Distribution of Replicate Results Around Decision Level for Sulfate Qualifications Tests

Decision Concentration - 400 ppm

| | Sample Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| Ring Oven Results | 40 | 200 | 600 | 1200 |
| Both ≥ 400(1) | 0 | 1 | 6 | 15 |
| Both < 400(2) | 15 | 10 | 2 | 0 |
| Other(3) | 0 | 4 | 7 | 0 |

(1) The ion concentration is deemed unacceptable.

(2) The ion concentration is deemed acceptable.

(3) More measurement is required before a decision can be made.

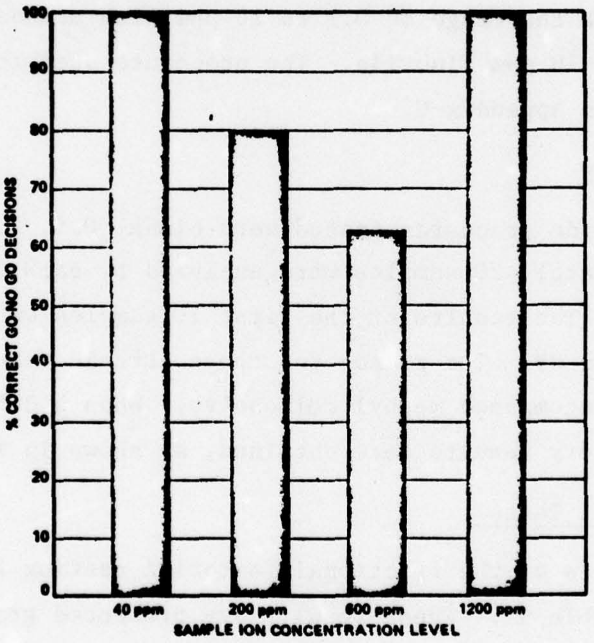


Figure 21. Percent Correct "Go-No Go" Decisions for Sulfate (Based on a decision concentration of 400 ppm)

significant effects are shown for varying experimental conditions for this test, with only turbidity and interaction of turbidity-ion concentration exhibiting a significant effect.

At the two extreme concentrations tested, 30 out of 30 paired results placed the water concentration on the correct side of the decision concentration level. At levels bracketing either side of the decision concentration, only three pairs of results were placed on the wrong side of the decision level. As a method for screening natural waters for sulfate, then, the ring oven method is feasible.

### 5.1.9 Fluoride

The reaction of thorium chloranilate with the fluoride ion forms the basis for the ring oven technique developed for this ion. Although phosphate also reacts with this reagent, this only occurs at phosphate concentrations in excess of those which would render the water unpotable because of high $PO_4$ levels. The reagent was evaluated during the previous contract effort over the range of 0.1 to 10 ppm with standard values of blank, 0.1, 1.0 and 10 ppm fluoride. The procedure used for fluoride analysis is given in Appendix C.

#### Operator Variability

The fluoride standards tested were blank, 0.5, 1.5 and 5 ppm fluoride. Approximately 20 samples were analyzed by each operator in groups of 10 each. The results of the first 10 samples were erratic, as can be seen in Table 89. The reason for these erratic results was found to be a bottle of decomposed methyl cellosolve. When a different bottle was used, satisfactory results were obtained, as shown in Table 90.

#### Fractional Factorial Tests

The results of the fractional factorial testing for the fluoride ion are given in Table 91. These results are presented graphically in Figure 22. Tables 92(a), (b) and (c) give the data resulting from the statistical analysis of this testing. The only highly significant effect for all observations was ion concentration (indicated with a double star). This was confirmed by both analyses using different residual mean square

## TABLE 89. Operator Variability Tests - Fluoride, Run No. 1

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| A | 1.7 | Blank | Blank |
| B | 0.6 | 0.5 | Blank |
| C | 0.4 | Blank | Blank |
| D | 6.0 | 5.0 | 2.0 |
| E | 0.6 | Blank | Blank |
| F | 1.7 | Blank | 0.3 |
| G | 6.0 | 5.0 | 0.5 |
| H | 1.7 | 1.0 | Blank |
| I | 0.6 | Blank | Blank |
| J | 0.4 | Blank | Blank |

50 µl samples
Standards: Blank - 0.5 - 1.5 - 5.0

---

## TABLE 90. Operator Variability Tests - Fluoride, Run No. 2

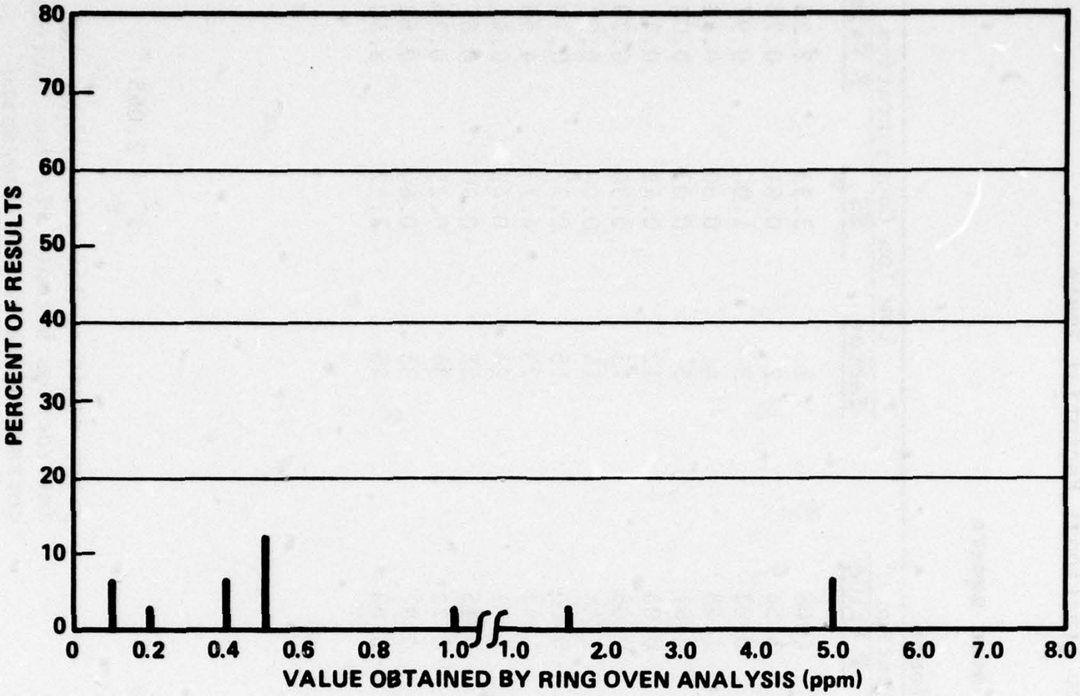
| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| K | 5.0 | 0.5 | 2.0(3.0)* |
| L | 0.1 | 0.4 | 0.1 |
| M | 1.5 | 0.5 | 0.5 |
| N | 1.0 | 0.5 | 0.5 |
| O | 0.1 | Blank | 0.3 |
| P | Blank | 0.5 | 1.5(1.5) |
| Q | 0.5 | 1.5 | 0.3 |
| R | 0.5 | Blank | 0.1(0.4) |
| S | 0.6 | 0.5 | 0.5 |
| T | 1.5 | 0.5 | 3.0(2.0) |

50 µl samples
Standards: Blank - 0.5 - 1.5 - 5.0

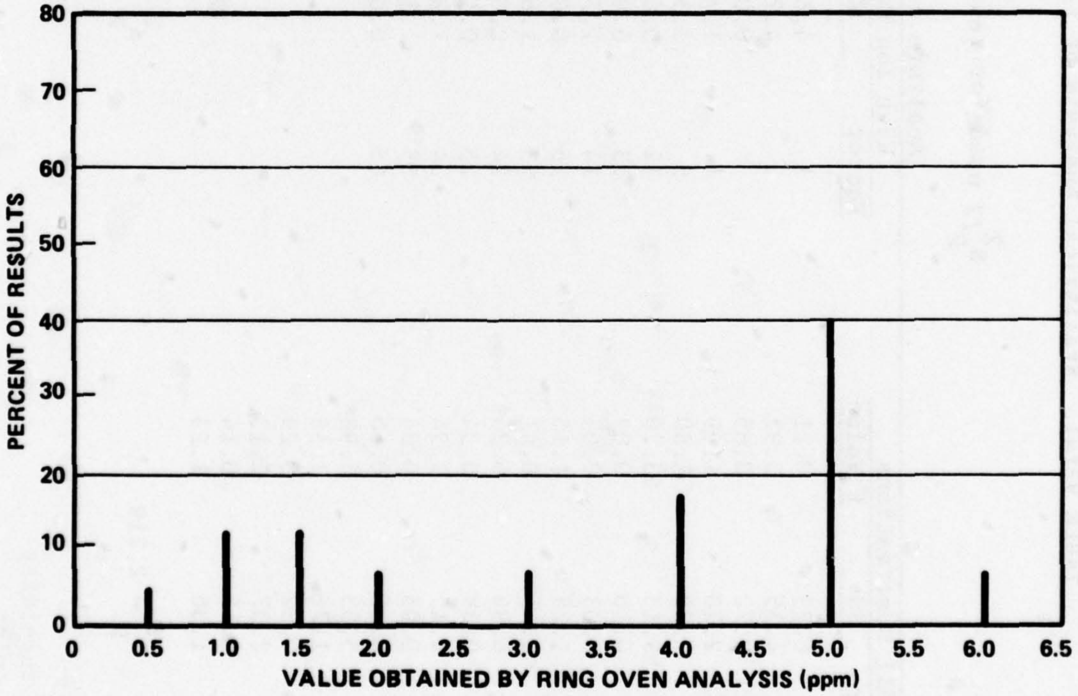
TABLE 91. Results of Fluoride Fractional Factorial Tests (Refer to Table 11. p. 26, for actual sample content.)

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 0.4 | 0.4 | 1.5 |
| b | 0.4 | Blank | Blank |
| c | 0.4 | Blank | Blank |
| d | 0.4 | 0.1 | 0.5 |
| e | 0.4 | 0.5 | 0.2 |
| f | 6.0 | 1.0 | 4.0 |
| g | 0.4 | 1.0 | 5.0 |
| h | 0.4 | 0.4 | Blank |
| i | 6.0 | 5.0 | 2.0 |
| j | 6.0 | 3.0 | 4.0 |
| k | 0.4 | 0.1 | Blank |
| l | 6.0 | 5.0 | >5.0 |
| m | 6.0 | 5.0 | 1.5 |
| n | 0.4 | Blank | 0.5 |
| o | 0.4 | Blank | Blank |
| p | 6.0 | 5.0 | 4.0 |
| q | 0.4 | Blank | Blank |
| r | 6.0 | 0.4 | 4.0 |
| s | 6.0 | 3.0 | 1.5 |
| t | 6.0 | >5.0 | 5.0 |
| u | 0.4 | Blank | 0.5 |
| v | 0.4 | Blank | Blank |
| w | 6.0 | 5.0 | 1.0 |
| x | 0.4 | Blank | 5.0 |
| y | 6.0 | 1.0 | 1.5 |
| z | 0.4 | Blank | Blank |
| aa | 6.0 | 5.0 | 5.0 |
| bb | 0.4 | Blank | Blank |
| cc | 6.0 | 1.0 | 1.5 |
| dd | 6.0 | 5.0 | 5.0 |
| ee | 6.0 | 5.0 | 4.0 |
| ff | 6.0 | 2.0 | 5.0 |

Standards: Blank - 0.5 - 1.5 - 5
Operator No. 4



ACTUAL VALUE 0.4ppm FLUORIDE



ACTUAL VALUE 6.0ppm FLUORIDE

Figure 22. Percent Distribution of Fluoride Fractional Factorial Test Results at Tested Ion Concentrations

## TABLE 92(a). Statistical Analysis of Fluoride Fractional Factorial Tests

$S_p^2/2$ used for residual mean square

Analysis of Variance

| All Observations | | | High Ion Concentration | | | Low Ion Concentration | | |
|---|---|---|---|---|---|---|---|---|
| **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** |
| 1 | 0.23 | 0.21 | 1 | 4.84 | 4.08 | 1 | 2.33 | 2.25 |
| 2 | 4.35 | 3.92 | 2 | 4.20 | 3.54 | 2 | 0.81 | 0.78 |
| 3 | 0.72 | 0.65 | 3 | 0.04 | 0.03 | 3 | 1.00 | 0.97 |
| 4 | 2.20 | 1.99 | 4 | 1.76 | 1.48 | 4 | 0.60 | 0.58 |
| 5 | 2.00 | 1.80 | 5 | 3.33 | 2.81 | 5 | 0.03 | 0.03 |
| 6 | 59.13 | 53.29** | 12 | 0.04 | 0.03 | 12 | 0.42 | 0.41 |
| 12 | 0.10 | 0.09 | 13 | 0.09 | 0.08 | 13 | 0.30 | 0.29 |
| 13 | 0.03 | 0.03 | 14 | 1.76 | 1.48 | 14 | 0.08 | 0.07 |
| 14 | 1.28 | 1.15 | 15 | 0.01 | 0.00 | 15 | 0.77 | 0.74 |
| 15 | 0.45 | 0.41 | 23 | 1.69 | 1.42 | 23 | 4.73 | 4.58* |
| 16 | 6.94 | 6.25* | 24 | 2.03 | 1.71 | 24 | 0.42 | 0.41 |
| 23 | 0.38 | 0.34 | 25 | 0.18 | 0.15 | 25 | 0.90 | 0.87 |
| 24 | 2.15 | 1.94 | 34 | 7.98 | 6.72* | 34 | 0.25 | 0.24 |
| 25 | 0.95 | 0.85 | 35 | 1.16 | 0.97 | 35 | 0.64 | 0.62 |
| 26 | 0.66 | 0.60 | 45 | 0.09 | 0.08 | 45 | 3.52 | 3.40 |
| 34 | 5.53 | 4.98* | | | | | | |
| 35 | 1.76 | 1.58 | | | | | | |
| 36 | 0.32 | 0.29 | | | | | | |
| 45 | 2.37 | 2.13 | | | | | | |
| 46 | 0.15 | 0.14 | | | | | | |
| 56 | 1.36 | 1.23 | | | | | | |
| $S_p^2 = 2.219$ | | | $S_p^2 = 2.37$ | | | $S_p^2 = 2.065$ | | |

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 92(b). Statistical Analysis of Fluoride Fractional Factorial Tests

### Analysis of Variance - All Observations

Residual Mean Square = 1.20506†

| Factor | SS | F Value |
|---|---|---|
| 1 | 0.23 | 0.19 |
| 2 | 4.35 | 3.61 |
| 3 | 0.72 | 0.60 |
| 4 | 2.20 | 1.83 |
| 5 | 2.00 | 1.66 |
| 6 | 59.13 | 49.07** |
| 12 | 0.10 | 0.08 |
| 13 | 0.03 | 0.03 |
| 14 | 1.28 | 1.06 |
| 15 | 0.45 | 0.37 |
| 16 | 6.94 | 5.76* |
| 23 | 0.38 | 0.32 |
| 24 | 2.15 | 1.79 |
| 25 | 0.95 | 0.78 |
| 26 | 0.66 | 0.55 |
| 34 | 5.53 | 4.59 |
| 35 | 1.76 | 1.46 |
| 45 | 2.37 | 1.96 |
| 46 | 0.15 | 0.13 |
| 56 | 1.36 | 1.13 |

†For this table, the lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

TABLE 92(c). Statistical Aanlysis of Fluoride Fractional Factorial Tests

The Average Errors for the High and Low Levels of Each Factor Are:
(Measured ion level minus actual ion level)

|  | High | Low |
|---|---|---|
| 1 | -1.212 | -1.044 |
| 2 | -1.497 | -0.759 |
| 3 | -1.278 | -0.978 |
| 4 | -1.391 | -0.866 |
| 5 | -0.878 | -1.378 |
| 6 | -2.487 | 0.231 |

(For all observations)

|  | High | Low |
|---|---|---|
| 1 | -3.037 | -1.938 |
| 2 | -3.000 | -1.975 |
| 3 | -2.537 | -2.438 |
| 4 | -2.819 | -2.156 |
| 5 | -2.031 | -2.944 |

(At the high ion concentration)

|  | High | Low |
|---|---|---|
| 1 | 0.612 | -0.150 |
| 2 | 0.006 | 0.456 |
| 3 | -0.019 | 0.481 |
| 4 | 0.038 | 0.425 |
| 5 | 0.275 | 0.187 |

(At the low ion concentration)

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

values. In addition, average error was lower at the low ion value, which again confirmed the effect due to varying ion value. Other significant effects (denoted by single stars) were seen from the interactions of turbidity-ion concentration and detection reagent temperature-age. The effects for all observations are summarized in Table 93.

## Qualification Tests

The results of the qualifications test for fluorides are given in Table 94. In Table 95 are found the data from the blank tests for fluorides. Figure 23 shows the permanent standard rings used for the qualifications testing.

For fluoride, the standards were blank, 0.5, 1.5 and 5. The ion concentrations used were 0.4, 0.6, 1.7 and 6.0. For this ion the data are so inconsistent that any analysis seemed rather pointless. The results are presented as Table 96. It was thought that deletion of the results for the high TDS water samples, which gave grossly erroneous results, might give a more promising statistical evaluation. With the high TDS water sample deleted, results are given in Table 96(a). Even with the more erroneous results deleted, the statistical analysis showed the fluoride test to be of insufficient accuracy.

The results of the blank tests, too, showed widely varying values. Although some color is obtained in the ring even with deionized water, it is apparent that some contamination occurred in the preparation of the blank test samples. Time was not available, however, to locate the source of this contamination.

## Conclusions

The difficulties encountered in the fluoride qualifications tests may be due to several factors. It was at first thought that high pH was causing the extremely high numbers obtained on some samples, such as those made from high TDS water. When the pH was adjusted to near neutrality, however, high values were still obtained.

Thought was also given to the possiblity of errors in the analysis of the original natural water samples for fluoride, which might cause the

TABLE 93. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Fluoride

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | - | - | - | - | - | * |
| Color | - | - | - | * | - | - |
| Detection Reagent Temperature | - | - | * | - | - | - |
| Reagent Age | - | * | - | - | - | - |
| Chlorine Concentration | - | - | - | - | - | - |
| Ion Concentration | * | - | - | - | - | ** |

- = no significant effect
* = significant effect
** = highly significant effect

TABLE 94. Fluoride Qualifications Tests

Standards: Blank - 0.5 - 1.5 - 5

| Water Sample | Operator | Measurement | Ion Concentration | | | |
|---|---|---|---|---|---|---|
| | | | 0.4 ppm | 0.6 ppm | 1.7 ppm | 6.0 ppm |
| Turbid | 1 | 1 | 5.0 | 0.5 | Blank | 0.4 |
| | | 2 | 5.0 | 5.0 | 5.0 | 4.0 |
| | 2 | 1 | 4.0 | Blank | 2.5 | 6.0 |
| | | 2 | 6.0 | 6.0 | 6.0 | 5.0 |
| | 3 | 1 | 1.0 | 5.0 | 3.0 | 7.0 |
| | | 2 | 5.0 | 7.0 | 3.0 | 5.0 |
| High TDS | 1 | 1 | 7.0 | 7.0 | 7.0 | 7.0 |
| | | 2 | 7.0 | 7.0 | 7.0 | 7.0 |
| | 2 | 1 | 10.0 | 15.0 | 12.0 | 14.0 |
| | | 2 | 14.0 | 10.0 | 7.0 | 11.0 |
| | 3 | 1 | 10.0 | 10.0 | 10.0 | 10.0 |
| | | 2 | 10.0 | 10.0 | 10.0 | 10.0 |
| Colored | 1 | 1 | Blank | Blank | Blank | Blank |
| | | 2 | 0.1 | Blank | Blank | 1.3 |
| | 2 | 1 | Blank | Blank | Blank | 0.6 |
| | | 2 | 0.5 | 1.2 | Blank | 0.3 |
| | 3 | 1 | Blank | Blank | Blank | Blank |
| | | 2 | 0.2 | Blank | 0.3 | 10.0 |
| Well | 1 | 1 | 0.5 | 0.6 | 0.5 | 5.0 |
| | | 2 | Blank | 4.9 | 0.4 | 5.0 |
| | 2 | 1 | 0.2 | Blank | 0.6 | 6.0 |
| | | 2 | 1.2 | 1.0 | 0.3 | 1.0 |
| | 3 | 1 | 0.2 | 0.7 | 4.0 | 1.0 |
| | | 2 | 0.3 | Blank | 1.5 | 2.0 |
| Organically Polluted | 1 | 1 | 1.3 | 0.8 | 0.2 | 1.5 |
| | | 2 | Blank | 0.3 | 1.4 | 4.5 |
| | 2 | 1 | 0.3 | 0.3 | Blank | 6.0 |
| | | 2 | 2.0 | 2.5 | 4.0 | 3.0 |
| | 3 | 1 | 1.7 | 0.7 | Blank | 2.0 |
| | | 2 | 0.3 | 0.0 | 7.0 | 5.0 |

## TABLE 95. Fluoride - Blank Tests (ppm)

(All samples consisted of deionized water)

| Operator 1 | Operator 2 | Operator 3 |
|---|---|---|
| 4.0 | 1.5 | 0.2 |
| 0.1 | 2.0 | 2.0 |
| 4.5 | 1.0 | 2.0 |
| 1.3 | 5.0 | 3.0 |
| 0.3 | 6.0 | 3.0 |
| 0.5 | 1.0 | 0.5 |
| 3.0 | 1.0 | 2.0 |
| 1.2 | 3.0 | 3.0 |
| 0.2 | 10.0 | 1.0 |
| 4.0 | 3.0 | 3.0 |
| 0.8 | 0.7 | 3.0 |
| 1.5 | 4.0 | 0.7 |
| 0.4 | 5.0 | 0.5 |
| 1.5 | 4.0 | 2.0 |
| 0.1 | 4.0 | 3.0 |

Figure 23. Fluoride Rings

## TABLE 96. Analysis of Qualifications Tests - Fluoride Ion
(Refer to Section 4.4 for explanation of terms)

### Analysis of Variance - All Ion Concentrations

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 37.361 | 2 | 18.681 | 4.737* |
| Ion Level | 312.602 | 3 | 104.201 | 60.895** |
| Water Sample | 1,240.148 | 4 | 310.037 | 32.924** |
| OPXIONLEV | 10.267 | 6 | 1.711 | 0.434 |
| OPXWATSAM | 75.335 | 8 | 9.417 | 2.388* |
| WATSMXIONL | 31.968 | 12 | 2.664 | 0.676 |
| Precision | 236.610 | 60 | 3.944 | |

$S_p^2 = 3.944$

$S_o^2 = 0.368$

Third order interaction MS = 3.214

### Average Errors of Measurement
(Measured Ion Concentration Minus Actual Ion Concentration)

| | Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| Operator | Blank | 1 | 2 | 6 |
| 1 | 2.19 | 2.01 | 0.45 | -2.43 |
| 2 | 3.42 | 3.00 | 1.54 | -0.71 |
| 3 | 2.47 | 2.74 | 2.18 | -0.80 |
| Water Sample | | | | |
| Turbid | 3.93 | 3.32 | 1.55 | -1.43 |
| High TDS | 9.27 | 9.23 | 7.13 | 3.83 |
| Colored | -0.27 | -0.40 | -1.65 | -3.97 |
| Well | 0.00 | 0.60 | -0.48 | -2.67 |
| Organically Polluted | 0.53 | 0.17 | 0.40 | -2.33 |

| | Operator | | |
|---|---|---|---|
| Water Sample | 1 | 2 | 3 |
| Turbid | 0.94 | 2.26 | 2.32 |
| High TDS | 4.82 | 9.45 | 7.82 |
| Colored | -2.00 | -1.85 | -0.86 |
| Well | -0.06 | -0.89 | -0.96 |
| Organically Polluted | -0.92 | 0.09 | -0.09 |

Table 96. (Continued)

## Analysis of Variance for Each Ion Concentration

The ion concentration is blank

| Source | SS | DF | MS | F | |
|---|---|---|---|---|---|
| Operator | 8.313 | 2 | 4.156 | 2.827 | $S_p^2 = 1.470$ |
| Water Sample | 392.565 | 4 | 98.141 | 34.239** | $S_o^2 = 0^{(1)}$ |
| OPXWATSAM | 22.931 | 8 | 2.866 | 1.950 | $\overline{X} = 2.693$ |
| Precision | 22.050 | 15 | 1.470 | | |

The ion concentration is 1 ppm

| Source | SS | DF | MS | F | |
|---|---|---|---|---|---|
| Operator | 5.269 | 2 | 2.634 | 0.704 | $S_p^2 = 3.742$ |
| Water Sample | 380.607 | 4 | 95.152 | 16.161** | |
| OPXWATSAM | 47.101 | 8 | 5.888 | 1.574 | $S_o^2 = 0^{(1)}$ |
| Precision | 56.125 | 15 | 3.742 | | $\overline{X} = 3.583$ |

The ion concentration is 2 ppm

| Source | SS | DF | MS | F | |
|---|---|---|---|---|---|
| Operator | 15.302 | 2 | 7.651 | 1.699 | $S_p^2 = 4.504$ |
| Water Sample | 280.455 | 4 | 70.114 | 44.220** | |
| OPXWATSAM | 12.685 | 8 | 1.586 | 0.352 | $S_o^2 = 0^{(1)}$ |
| Precision | 67.565 | 15 | 4.504 | | $\overline{X} = 3.390$ |

The ion concentration is 6 ppm

| Source | SS | DF | MS | F | |
|---|---|---|---|---|---|
| Operator | 18.745 | 2 | 9.372 | 1.547 | $S_p^2 = 6.058$ |
| Water Sample | 218.488 | 4 | 54.622 | 6.265* | |
| OPXWATSAM | 69.752 | 8 | 8.719 | 1.439 | $S_o^2 = 0^{(1)}$ |
| Precision | 90.870 | 15 | 6.058 | | $\overline{X} = 4.687$ |

(1) If the F value for operator effect is not significant, $S_o^2$ is taken to be zero.

## TABLE 96. (Continued)

### Average Errors for Individual Factors

| Operator | Average Error |
|---|---|
| 1 | 0.555 |
| 2 | 1.812 |
| 3 | 1.647 |
| **Water Sample** | |
| Turbid | 1.842 |
| High TDS | 7.367 |
| Colored | -1.571 |
| Well | -0.637 |
| Organically Polluted | -0.308 |
| **Ion Concentration** | |
| Blank | 2.693 |
| 1 ppm | 2.583 |
| 2 ppm | 1.390 |
| 6 ppm | -1.313 |

## TABLE 96(a). Analysis of Qualifications Tests - Fluoride Ion (With High TDS Water Sample Deleted)

(Refer to Section 4.4 for explanation of terms)

### Analysis of Variance - All Ion Concentrations

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 6.312 | 2 | 3.156 | 0.761 |
| Ion Level | 206.367 | 3 | 68.789 | 38.701 |
| Water Sample | 149.924 | 3 | 49.975 | 16.385 |
| OPXIONLEV | 10.665 | 6 | 1.777 | 0.428 |
| OPXWATSAM | 18.301 | 6 | 3.050 | 0.735 |
| WATSMXIONL | 20.402 | 9 | 2.267 | 0.546 |
| Precision | 199.110 | 48 | 4.148 | |

$s_p^2 = 4.148$

$s_o^2 = 0^{(1)}$

Third order Interaction MS = 3.805

### Average Errors of Measurement

(Measured Ion Concentration Minus Actual Ion Concentration)

| | Ion Concentration (ppm) | | | |
|---|---|---|---|---|
| Operator | Blank | 1 | 2 | 6 |
| 1 | 1.09 | 0.91 | -0.76 | -3.29 |
| 2 | 1.37 | 0.77 | -0.02 | -2.51 |
| 3 | 0.69 | 1.07 | 0.65 | -2.00 |
| Water Sample | | | | |
| Turbid | 3.93 | 3.32 | 1.55 | -1.43 |
| Colored | -0.27 | -0.40 | -1.65 | -3.97 |
| Well | 0.00 | 0.60 | -0.48 | -2.67 |
| Organically Polluted | 0.53 | 0.17 | 0.40 | -2.33 |

| | Operator | | |
|---|---|---|---|
| Water Sample | 1 | 2 | 3 |
| Turbid | 0.94 | 2.26 | 2.32 |
| Colored | -2.00 | -1.85 | -0.86 |
| Well | -0.06 | -0.89 | -0.96 |
| Organically Polluted | -0.92 | 0.09 | -0.09 |

TABLE 96(a). (Continued)

## Analysis of Variance for Each Ion Concentration

The ion concentration is blank

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 1.908 | 2 | 0.954 | 0.815 |
| Water Sample | 68.500 | 3 | 22.833 | 34.229 |
| OPXWATSAM | 4.003 | 6 | 0.667 | 0.570 |
| Precision | 14.050 | 12 | 1.171 | |

$S_p^2 = 1.171$

$S_o^2 = 0$(1)

$\overline{X} = 1.050$

The ion concentration is 1 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 0.361 | 2 | 0.180 | 0.050 |
| Water Sample | 48.938 | 3 | 16.313 | 4.515 |
| OPXWATSAM | 21.676 | 6 | 3.613 | 0.994 |
| Precision | 43.625 | 12 | 3.635 | |

$S_p^2 = 3.635$

$S_o^2 = 0$(1)

$\overline{X} = 1.921$

The ion concentration is 2 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 7.986 | 2 | 3.993 | 0.870 |
| Water Sample | 33.061 | 3 | 11.020 | 6.840 |
| OPXWATSAM | 9.668 | 6 | 1.611 | 0.351 |
| Precision | 55.065 | 12 | 4.589 | |

$S_p^2 = 4.589$

$S_o^2 = 0$(1)

$\overline{X} = 1.954$

The ion concentration is 6 ppm

| Source | SS | DF | MS | F |
|---|---|---|---|---|
| Operator | 6.722 | 2 | 3.361 | 0.467 |
| Water Sample | 19.827 | 3 | 6.609 | 0.771 |
| OPXWATSAM | 51.441 | 6 | 8.573 | 1.191 |
| Precision | 86.370 | 12 | 7.197 | |

$S_p^2 = 7.197$

$S_o^2 = 0$(1)

$\overline{X} = 5.692$

(1) If the F value for operator effect is not significant, $S_o^2$ is tkane to be zero.

### TABLE 96(a). (Continued)

### Average Errors for Individual Factors

| Operator | Average Error |
|---|---|
| 1 | -0.512 |
| 2 | -0.097 |
| 3 | -0.103 |
| **Water Sample** | |
| Turbid | 1.842 |
| Colored | -1.571 |
| Well | -0.637 |
| Organically Polluted | -0.308 |
| **Ion Concentration** | |
| Blank | 1.050 |
| 1 ppm | 0.921 |
| 2 ppm | -0.046 |
| 6 ppm | -2.600 |

erratic ring oven results. Unfortunately, time did not allow for re-analysis of the natural water samples; however, incorrect original analysis would not explain the difference in duplicate analysis of ring oven samples, such as those obtained for turbid water, Operator No. 1, 0.6 ppm concentration; and well water, Operator No. 2, 6 ppm concentration.

The ring oven fluoride test uses a reagent-sample mixture in a vial. It was observed during the qualifications testing that those samples giving inordinately high results, such as the TDS samples, were not settling in the same manner as those samples giving correct results. It was thought that the total dissolved solids level itself was the possible cause of the non-settling. In addition, as can be observed from Table 15 (p. 39), all of the natural water samples except for the turbid sample had a TDS level in excess of 200 mg/l. This, however, does not explain the high fluoride levels frequently obtained on the turbid water samples.

Another factor which may have had an effect on the fluoride results are the standard values themselves. Fluoride rings are very pale, and the standards selected in this study allowed for a very minimal gradation. It is possible that, with use of more widely differing standards, better results could have been obtained.

These are some of the factors considered in an effort to account for the poor fluoride qualifications test results. The fluoride test is believed to be much better than the results of the qualifications test indicated, especially when one considers the relatively satisfactory results of the fractional factorial tests which showed only one highly significant effect due to ion concentration. It does not appear suitable, however, for use at this time for monitoring natural waters.

### 5.1.10 Nitrate

The nitrate range evaluated during the previous contractual effort was from 1 to 20 ppm nitrate. The initial standard values were 1, 5, 10 and 20 ppm, with the selected reagent being N,N-diphenylbenzidine in sulfuric acid. The procedure developed using this reagent, which was used for all testing is given in Appendix C. The diphenylbenzidine reagent will react with any oxidizing agent, including nitrite.

## Operator Variability Tests

The four standard values selected were 5, 10, 20 and 30 ppm nitrate. Twelve samples were then analyzed by two operators and compared to these standard values. The results are given in Table 97 and were almost uniformly too high. In an attempt to improve reliability, sample size was increased to 30 μl, with the results given in Table 98. The results were somewhat improved, but erratic points still occurred.

It was then decided to check the possibility that erratic results were due to variances in operator experience between the operators who prepared the samples and the project chemist who prepared the standards. Each operator prepared the standard rings for the other operator's use, and sample analysis was performed. Results are presented in Table 99 and were basically satisfactory.

Thus the standard values of 5, 10, 20 and 30 ppm nitrate were submitted to the Army for approval as permanent standards. The Army requested that the 10 ppm decision level be bracketed more closely if possible. For this reason, the standard values of 6, 10, 14 and 25 ppm were used in permanent standards and for all subsequent testing.

## Fractional Factorial Tests

Two sets of fractional factorial tests were performed for the nitrate ion. The first, the results of which are given in Table 100 and are displayed graphically in Figure 24, was performed using actual standards prepared by the project chemist. The statistical analysis of these results is given in Tables 101(a), (b) and (c) and summarized in Table 102.

At the August 10th meeting between the Army and Atlantic Research, it was decided to repeat the $NO_3$ fractional factorial tests using a dye transfer print as the permanent standard. If the results from this set of tests were more satisfactory, then nitrate qualifications tests would be performed. Table 103 gives the results for these fractional factorial tests using permanent standards, while Figure 25 gives the results graphically. Figure 26 shows the permanent standard nitrate rings used in this testing.

## TABLE 97. Operator Variability Tests - Nitrate, Run No. 1

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| A | 15 | 30 | 30 |
| B | 20 | >30 | 30 |
| C | 10 | 30 | 20 |
| D | 20 | >30 | 5 |
| E | 30 | >30 | 25 |
| F | 30 | >30 | 20 |
| G | 15 | 30 | 20 |
| H | 5 | 20 | 10 |
| I | 10 | 20 | 15 |
| J | 15 | 20 | 20 |
| K | 5 | 10 | 10 |
| L | 10 | 20 | 8 |

15 µl Samples

Standards: 5-10-20-30 ppm

Decision Level: 10 ppm

## TABLE 98. Operator Variability Tests - Nitrate, Run No. 2

| Sample | Actual Concentration (ppm) | Ring Oven Results Operator No. 5 (ppm) | Ring Oven Results Operator No. 6 (ppm) |
|---|---|---|---|
| A | 15 | 20 | 20 |
| F | 30 | >30 | 20 |
| I | 10 | 10 | 15 |
| L | 10 | 5 | 20 |
| C | 10 | 15 | 25 |
| E | 30 | 30 | 25 |
| B | 20 | 5 | 20 |
| D | 20 | 20 | 30 |

30 µl Samples

Standards: 5-10-20-30

Decision Level: 10 ppm

## TABLE 99. Operator Variability Tests - Nitrate, Run No. 3

| Sample | Concentration (ppm) | Ring Oven Results Operator No. 5 Stnds by Operator No. 6 (ppm) | Ring Oven Results Operator No. 6 Stnds by Operator No. 5 (ppm) |
|---|---|---|---|
| L | 10 | 10 | 10 |
| K | 5 | 5 | 5 |
| J | 15 | 15 | 15 |
| I | 10 | 15 | 10 |
| H | 5 | 10 | 5 |
| G | 15 | 18 | 15 |
| F | 30 | >30 | 30 |
| E | 30 | >30 | 30 |
| D | 20 | 30 | 20 |
| C | 10 | 20 | 10 |
| B | 20 | 30 | 20 |
| A | 15 | 20 | 15 |

15 μl Samples

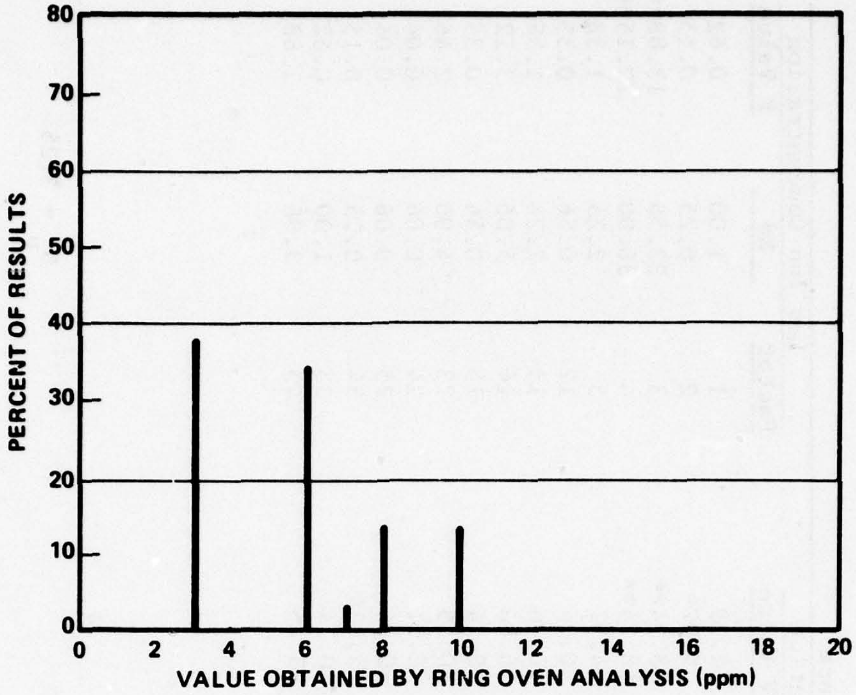
Standards: 5-10-20-30

Decision Level: 10 ppm

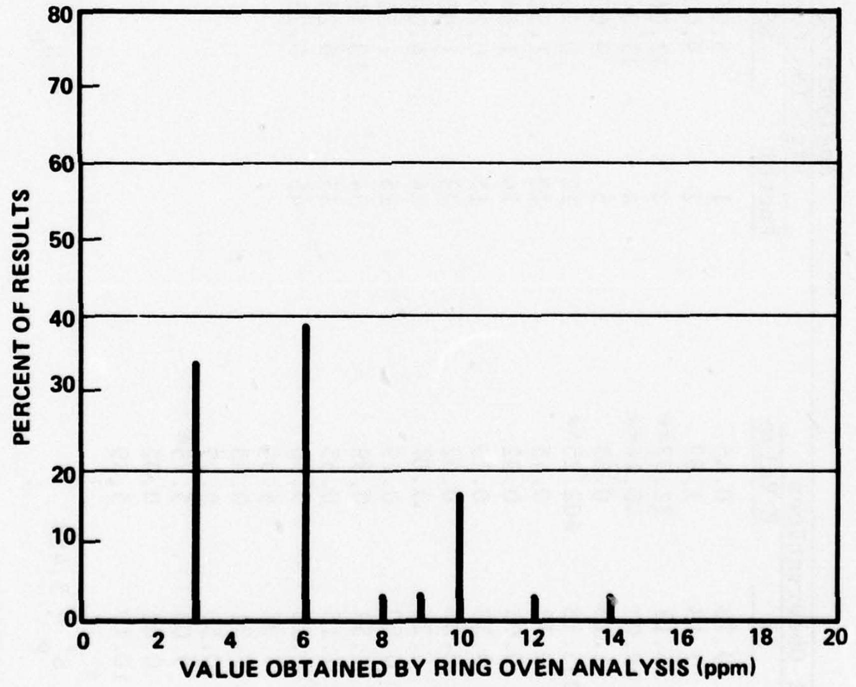
TABLE 100. Results of Nitrate Fractional Factorial Tests - I (Refer to Table 11, p. 26 for actual sample content.)

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 4 | 10 | 10 |
| b | 4 | 8 | 7 |
| c | 4 | 6 | 6 |
| d | 4 | 6 | 10 |
| e | 4 | 6 | 8 |
| f | 16 | 14 | 9 |
| g | 4 | <6 | 8 |
| h | 4 | <6 | 6 |
| i | 16 | 12 | 8 |
| j | 16 | 10 | 10 |
| k | 4 | 6 | 6 |
| l | 16 | <6 | <6 |
| m | 16 | 6 | 10 |
| n | 4 | 10 | 8 |
| o | 4 | <6 | 6 |
| p | 16 | 6 | 6 |
| q | 4 | <6 | <6 |
| r | 16 | <6 | <6 |
| s | 16 | <6 | 6 |
| t | 16 | 6 | 10 |
| u | 4 | Blank | <6 |
| v | 4 | 6 | <6 |
| w | 16 | <6 | 6 |
| x | 4 | 6 | <6 |
| y | 16 | <6 | <6 |
| z | 4 | <6 | <6 |
| aa | 16 | <6 | <6 |
| bb | 4 | <6 | 6 |
| cc | 16 | <6 | 6 |
| dd | 16 | 6 | 6 |
| ee | 16 | 6 | 6 |
| ff | 16 | 6 | 10 |

Standards: 6 - 10 - 14 - 25
Operator No. 4



ACTUAL VALUE 4ppm NITRATE



ACTUAL VALUE 16ppm NITRATE

Figure 24. Percent Distribution of Nitrate I Fractional Factorial Test Results at Tested Ion Concentrations

TABLE 101(a). Statistical Analysis of Nitrate Fractional Factorial Tests - I

$S_p^2/2$ used for residual mean square

Analysis of Variance

| All Observations | | | High Ion Concentration | | | Low Ion Concentration | | |
|---|---|---|---|---|---|---|---|---|
| **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** | **Factor** | **SS** | **F Value** |
| 1 | 0.78 | 0.45 | 1 | 5.06 | 2.79 | 1 | 1.00 | 0.62 |
| 2 | 3.13 | 1.82 | 2 | 9.00 | 4.97* | 2 | 0.25 | 0.15 |
| 3 | 55.13 | 32.07** | 3 | 33.06 | 18.24** | 3 | 22.56 | 13.88** |
| 4 | 69.03 | 40.16** | 4 | 33.06 | 18.24** | 4 | 36.00 | 22.15** |
| 5 | 1.13 | 0.65 | 5 | 9.00 | 4.97 | 5 | 2.25 | 1.38 |
| 6 | 1,035.13 | 602.25** | 12 | 0.25 | 0.14 | 12 | 0.56 | 0.35 |
| 12 | 0.78 | 0.45 | 13 | 1.56 | 0.86 | 13 | 2.25 | 1.38 |
| 13 | 0.03 | 0.02 | 14 | 1.56 | 0.86 | 14 | 5.06 | 3.12 |
| 14 | 0.50 | 0.29 | 15 | 0.25 | 0.14 | 15 | 0.56 | 0.35 |
| 15 | 0.03 | 0.02 | 23 | 1.00 | 0.55 | 23 | 4.00 | 2.46 |
| 16 | 5.28 | 3.07 | 24 | 4.00 | 2.21 | 24 | 0.06 | 0.04 |
| 23 | 0.50 | 0.29 | 25 | 1.56 | 0.86 | 25 | 0.06 | 0.04 |
| 24 | 1.53 | 0.89 | 34 | 10.56 | 5.83* | 34 | 0.25 | 0.15 |
| 25 | 1.13 | 0.65 | 35 | 0.25 | 0.14 | 35 | 1.00 | 0.62 |
| 26 | 6.13 | 3.56 | 45 | 6.25 | 3.45 | 45 | 3.06 | 1.88 |
| 34 | 7.03 | 4.09 | | | | | | |
| 35 | 1.31 | 0.65 | | | | | | |
| 36 | 0.50 | 0.29 | | | | | | |
| 45 | 9.03 | 5.25* | | | | | | |
| 46 | 0.03 | 0.02 | | | | | | |
| 56 | 10.13 | 5.89 | | | | | | |
| $S_p^2 = 3.483$ | | | $S_p^2 = 3.625$ | | | $S_p^2 = 3.25$ | | |

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

## TABLE 101(b). Statistical Analysis of Nitrate Fractional Factorial Tests - I

### Analysis of Variance - All Observations

Residual Mean Square = 2.24375†

| Factor | SS | F Value |
|---|---|---|
| 1 | 0.78 | 0.35 |
| 2 | 3.13 | 1.39 |
| 3 | 55.13 | 24.57** |
| 4 | 69.03 | 30.77** |
| 5 | 1.13 | 0.50 |
| 6 | 1,035.13 | 461.34** |
| 12 | 0.78 | 0.35 |
| 13 | 0.03 | 0.01 |
| 14 | 0.50 | 0.22 |
| 15 | 0.03 | 0.01 |
| 16 | 5.28 | 2.35 |
| 23 | 0.50 | 0.22 |
| 24 | 1.53 | 0.68 |
| 25 | 1.13 | 0.50 |
| 26 | 6.13 | 2.73 |
| 34 | 7.03 | 3.13 |
| 35 | 1.13 | 0.50 |
| 36 | 0.50 | 0.22 |
| 45 | 9.03 | 4.03 |
| 46 | 0.03 | 0.01 |
| 56 | 10.13 | 4.51 |

†For this table, the lumped higher order interactions were used for the residual mean square.

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

A two digit number represents the interaction between the two factors corresponding to the composite digits; i.e., 24 = color interacting with reagent age.

* = significant effect
** = highly significant effect

### TABLE 101(c). Statistical Analysis of Nitrate Fractional Factorial Tests - I

The Average Errors for the High and Low Concentration of Each Factor Are:
(Measured Ion Concentration Minus Actual Ion Concentration)

|  | High | Low |
|---|---|---|
| 1 | -3.969 | -4.281 |
| 2 | -4.438 | -3.813 |
| 3 | -5.438 | -2.813 |
| 4 | -5.594 | -2.656 |
| 5 | -3.938 | -4.313 |
| 6 | -9.813 | 1.563 |

(All observations)

|  | High | Low |
|---|---|---|
| 1 | -9.250 | -10.375 |
| 2 | -10.563 | -9.063 |
| 3 | -11.250 | -8.375 |
| 4 | -11.250 | -8.375 |
| 5 | - 9.063 | -10.563 |

(At the high ion concentration)

|  | High | Low |
|---|---|---|
| 1 | 1.313 | 1.813 |
| 2 | 1.688 | 1.438 |
| 3 | 0.375 | 2.750 |
| 4 | 0.063 | 3.063 |
| 5 | 1.188 | 1.938 |

(At the low ion concentration)

1 = turbidity
2 = color
3 = reagent temperature
4 = reagent age
5 = chlorine concentration
6 = ion concentration

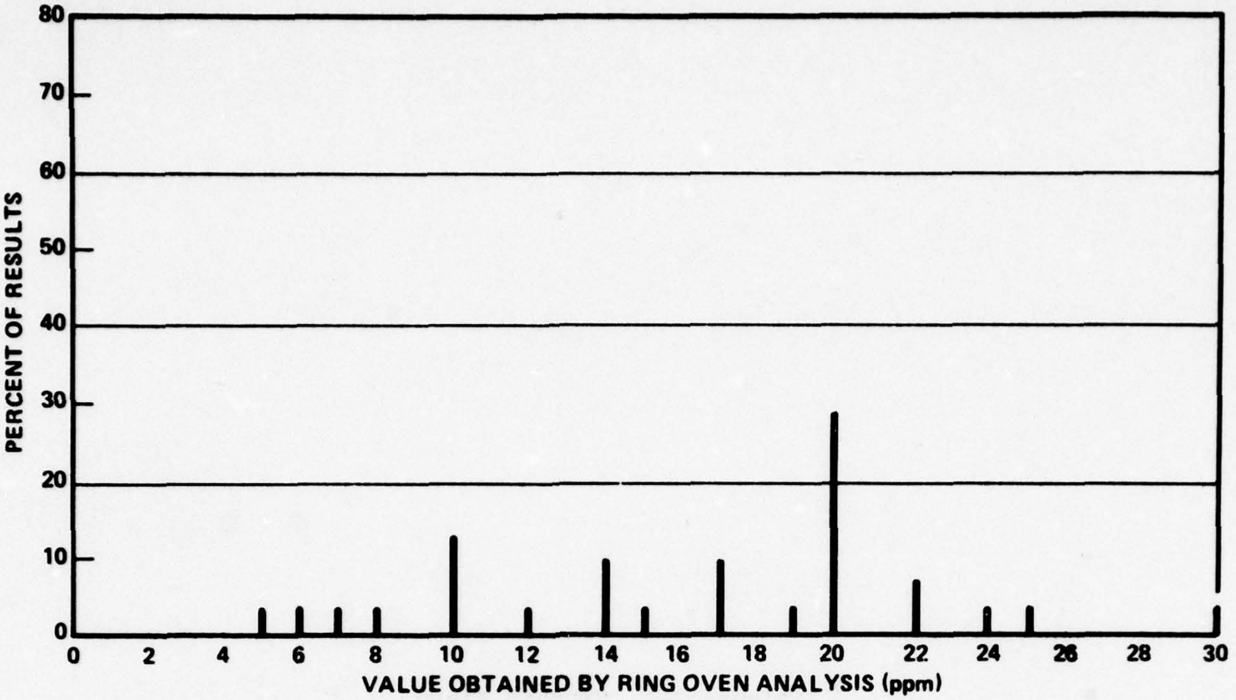
TABLE 102. Summary of Factor Effects for All Observations Encountered During Fractional Factorial Tests - Nitrate I

| | Turbidity | Color | Detection Reagent Temperature | Reagent Age | Chlorine Concentration | Ion Concentration |
|---|---|---|---|---|---|---|
| Turbidity | - | - | - | - | - | - |
| Color | - | - | - | - | - | - |
| Detection Reagent Temperature | - | - | ** | - | - | - |
| Reagent Age | - | - | - | ** | * | - |
| Chlorine Concentration | - | - | - | * | - | - |
| Ion Concentration | - | - | - | - | - | ** |

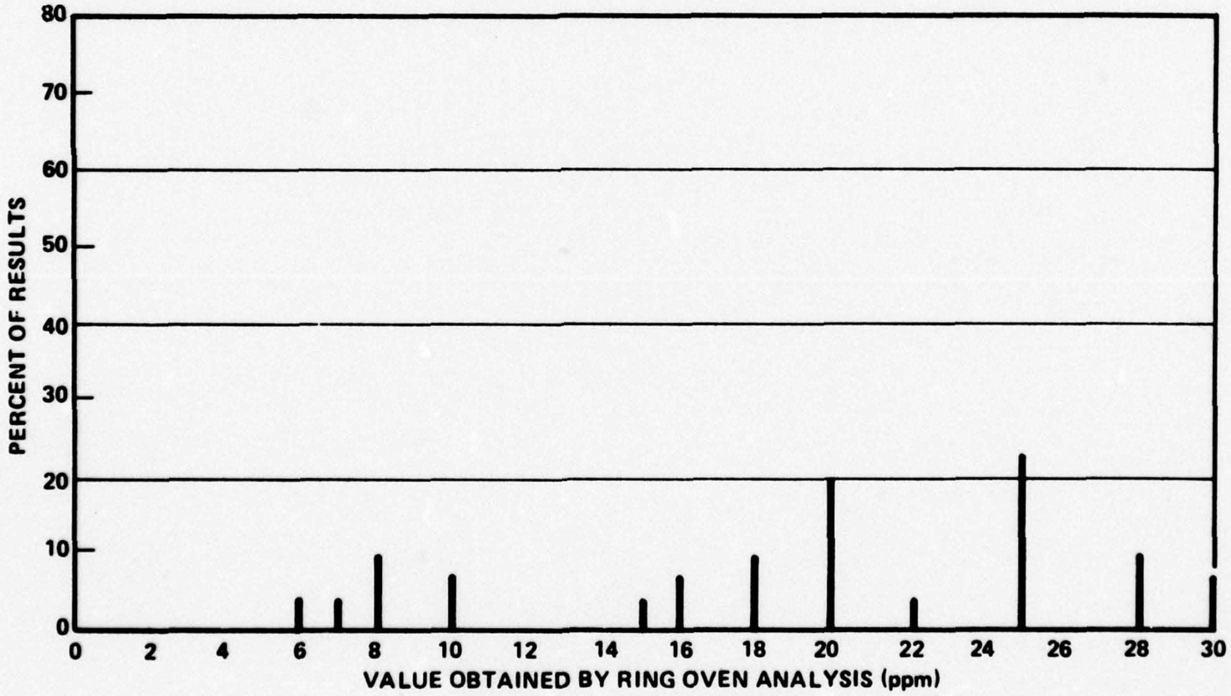
- = no significant effect
* = significant effect
** = highly significant effect

TABLE 103. Results of Nitrate Fractional Factorial Tests - II (Refer to Table 11, p. 26 for actual sample content.)

| Sample | Actual Concentration (ppm) | Ring Oven Results (ppm) | |
|---|---|---|---|
| a | 4 | 18 | 7 |
| b | 4 | 5 | 6 |
| c | 4 | 14 | 14 |
| d | 4 | 20 | 10 |
| e | 4 | 18 | 20 |
| f | 16 | 10 | 8 |
| g | 4 | 18 | 20 |
| h | 4 | 24 | 30 |
| i | 16 | 10 | 6 |
| j | 16 | 15 | 8 |
| k | 4 | 20 | 22 |
| l | 16 | 25 | 16 |
| m | 16 | 7 | 8 |
| n | 4 | 10 | 8 |
| o | 4 | 25 | 22 |
| p | 16 | 25 | 20 |
| q | 4 | 10 | 12 |
| r | 16 | 20 | 25 |
| s | 16 | 30 | 25 |
| t | 16 | 16 | 20 |
| u | 4 | 20 | 20 |
| v | 4 | 17 | 19 |
| w | 16 | 30 | 25 |
| x | 4 | 20 | 14 |
| y | 16 | 22 | 18 |
| z | 4 | 15 | 10 |
| aa | 16 | 18 | 20 |
| bb | 4 | 20 | 20 |
| cc | 16 | 20 | 20 |
| dd | 16 | 28 | 18 |
| ee | 16 | 25 | 28 |
| ff | 16 | 25 | 28 |



ACTUAL VALUE 4ppm NITRATE



ACTUAL VALUE 16ppm NITRATE

Figure 25. Percent Distribution of Nitrate II Fractional Factorial Test Results at Tested Ion Concentrations

Figure 26.  Nitrate Rings

It can be seen that the data in Table 103 are still erratic. Thus, neither statistical evaluation of these results nor qualifications testing of the nitrate ion was performed.

Conclusions

The problem with the nitrate test appears to be due to several factors:

1. Contaminated filter paper caused difficulties. Whatman 541 was unsuitable, having a high nitrate content. Whatman No. 40 filter paper, which was used for nitrate, was sporadically contaminated, even within a box. This is not surprising, considering that the Whatman 40 is double acid washed. Methods of cleaning filter papers should be investigated in order to solve this problem.
2. The nitrate test appears to be extremely sensitive to operator technique and experience. By far the best results were achieved when the operators prepared their own standards and compared them to rings treated simultaneously with regent. This alternative, however, is probably not feasibile for a field test kit.

## 5.2 Feasibility Study - General Ion Scans

### 5.2.1 Reagent Survey

Several reagents encountered during the previous contract effort appeared suitable for use as general scan reagents, particularly for the metals. Some of these are described briefly in the following paragraphs.

### 5.2.1.1 Cations

Dithizone

Dithizone (diphenylthiocarbazone) dissolves in chloroform to form a green solution which reacts with many metals to form colored metallic diphenylthiocarbazone complexes. Some of the metals which will react with dithizone include copper, iron, lead, zinc, mercury and cadmium.

**PAN**

1-(2-pyridylazo)naphthol (PAN), the zinc reagent used with the ring oven, should also prove useful as a general scanning reagent for metals. Iron, lead, copper, mercury, and cadmium, in addition to zinc, will react to form colored complexes with PAN.

**PAR**

4-(2-pyridylazo)resorcinol (PAR) is a colorimetric reagent for metals similar in action to PAN. Most of the metals which will react with PAN will also react with PAR, although in a less sensitive manner.

**TAN**

In the course of the work performed, the lead reagent, thiazolylazonaphthol (TAN) reacted with a variety of metals, in addition to lead. These metals included iron, copper, mercury and cadmium.

**Other Cation Reagents**

Many other general metal reagents would seem to have potential for ring oven application. These include hydroxyquinoline, toluene-3,4-dithiol, and quinalizarin.

### 5.2.1.2 Anions

**Silver Nitrate**

A modification of the $AgNO_3$-ultraviolet light procedure as used for chlorides would seem to show the greatest promise for total anion analysis. If a sample were applied, washed to the ring zone with deionized water, sprayed with $AgNO_3$, and exposed to UV-light, the resulting ring should serve as a good indication of the total anion content of the water.

**Barium Chloride**

Barium chloride will react with many anions to form water-insoluble precipitates. These precipitates can then be reacted with rhodizonoic acid, as in the sulfate test, to give a red-brown ring. Among the anions which form water insoluble precipitates with $Ba^{+2}$ are chromate, sulfate, carbonate, sulfite, borate, arsenate, and phosphate.

### 5.2.2 Laboratory Testing

#### Cations

A preliminary evaluation of the reagents for cations discussed above led to the selection of PAN, PAR and TAN for actual laboratory examination. All three were relatively sensitive and non-specific, important criteria for any general reagent. Dithizone was eliminated from consideration because of its tendency to produce strong background color, and because of the wide pH variations required for its color reactions to occur. Most of the other metal reagents such as hydroxyquinoline, form white precipitates with the metals in the course of reaction. Such reactions are not suitable for ring oven techniques.

One part-per-million solutions of the metals manganese, lead, mercury, cadmium, copper, selenium, iron, chromium, calcium, magnesium, zinc and barium, were prepared to be used as laboratory test solutions. A variety of experiments were then performed, using these solutions, stock 1000 ppm standard solutions, various wash solutions, and the PAN and PAR reagents. These experiments are discussed below.

In order to check the responsiveness of PAN versus PAR, 15 µl of the 1000 ppm solutions were applied and washed to the 22 mm ring zone with a dilute acid wash (HCl). Two rings were prepared for each ion. One ring was then sprayed with the PAN reagent and one with PAR (saturated in ethanol). Results were disappointing. Copper, lead, iron, manganese and zinc responded to PAN, but very faintly, while only copper and iron responded to PAR.

Earlier work with the zinc tests, however, had suggested that PAN was rather pH-sensitive, and an ammonium acetate (15%) dip was required in order to bring up the Zn colors in this test. An ammonium acetate bath was tried with the PAN- and PAR-treated rings, with some success in the case of PAN, but very little in the case of PAR.

Since ammonium acetate is required for a good color reaction with both PAN and PAR, ammonium acetate was tested as a wash solution. While the resulting rings did show definite color reactions, rings were extremely diffuse. This is to be expected when the relatively high pH of the ammonium acetate solution is considered, since many metals are insoluble in more basic solutions. For this reason, it was decided to use an initial acid wash, followed by an ammonium acetate wash before reagent application. In addition, it was decided to concentrate on PAN, as it appears to give stronger color reactions with more metals than PAR does.

Dilute nitric acid, prepared by fuming deionized water with $NO_2$, from concentrated $HNO_3$, was used as an acid solution, along with ammonium acetate to wash 50 μl of 1 ppm metals solution to the 22 mm ring zone. When PAN was applied, a positive reaction was given for Zn, Fe, Mn, Hg, Cu, and Pb.

In order to increase ring intensity and test sensitivity, this test was repeated, using only the 14 mm ring. Calcium, in addition to the above ions, showed a positive reaction; however, a very strong blank indicated contamination in one of the wash solutions. This proved to be the case, as rather large amounts of iron were found in the $HNO_3$. Hydrochloric acid (1% fumed Ultrex) was substituted as the acid wash. This proved to give a better blank, and Ca was found not to react with PAN.

To obtain a rough indication of the reagent sensitivity to the various metals, sample sizes were reduced, first to 15 μl of 1 ppm solution, then to 5 μl of 1 ppm solution, and washed to the 14 mm ring with 1% HCl and 15% ammonium acetate. With the 15 μl samples, positive reactions were obtained for Cd, Cu, Zn, Fe, Mn, Pb, and a very faint reaction for Hg. At the 5 μl sample size, however, the reactions were very faint for Hg, Cu, Mn, Fe, Zn and Pb, showing only minute difference from the blank. This indicated that a sensitivity below 1 ppm with 15 μl samples could not be obtained with this reagent.

Further tests were then performed with Cu, Zn, Fe, Cd, and Pb. Mercury and manganese did not react reproducibly enough with PAN, so these two metals were not tested. It was decided to match rings by intensities rather than by colors, as colors differed from one metal-PAN complex to the next. Black-and-white film was used to photograph the rings for intensity comparisons. The results of these tests, equating rings of equal intensity, are given in Table 104. A procedure which can be used for general scan analysis is given in Table 105.

As discussed above, it was apparent that for concentrations below 1 ppm, a reagent other than PAN would be required. Since the lead reagent, thiazolylazonaphthol (TAN) appeared extremely sensitive to various metals, this reagent was tested for metals at levels less than 1 ppm. Positive reactions were obtained with Zn, Mn, Cd, Pb, Cu and Fe. Results were not promising, as 50 µl samples were required in order to bring the metals within the sensitivity range. This sample size seems large when considered in the context of the simplicity and rapidity desirable for any general scan technique.

### 5.2.3 Anions

The only general scan reagent for anions considered was silver nitrate-ultraviolet light. This is due to the fact that the anion reactions most frequently used with the ring oven involve the production of a color by the precipitation of a metal salt; a color due either to the salt itself, or to a product liberated by the precipitation. The two metals most commonly used in qualitative analysis to give a variety of water-insoluble salts are barium and silver. While both of these are currently used by Atlantic Research in ring oven tests, it was decided that the use of silver would provide two advantages:

1. Greater simplicity. Only one reagent, $AgNO_3$, need be applied in addition to the water wash, in contrast to the $BaCl_2$ and the potassium rhodizonate required in the barium tests.
2. More silver salts are water-insoluble than the respective barium salts.

Tests were performed in the laboratory using standard solutions of the anions $F^-$, $Cl^-$, $SO_4^{=}$, $CN^-$, $PO_4^{\equiv}$ and $S^{=}$. The sample was applied to Whatman

## TABLE 104. General Scan Reagents - Response of Various Metals to PAN

(Each column contains rings of equivalent intensities)

| | | | |
|---|---|---|---|
| 0.5 µg Fe | 0.15 µg Fe | 2.0 µg Cd | 0.015 µg Zn |
| 0.5 µg Cu | 0.15 µg Cu | 0.05 µg Fe | 0.015 µg Fe |
| 0.25 µg Zn | 0.15 µg Zn | 2.50 µg Pb | 0.015 µg Cu |
| | | 0.05 µg Cu | 2.000 µg Pb |
| | | 0.05 µg Zn | |

(Rings below 2 µg of Cd and Pb did not appear reproducible enough for further examination with PAN)

## TABLE 105. General Scan Procedure for Cations

14 mm attachment

Whatman No. 40 Filter Paper

1. Apply sample. Dry.
2. Wash to ring zone with 15 µl 1% Ultrex hydrochloric acid.
3. Wash to ring zone with 15 µl 15% ammonium acetate. Dry.
4. Spray with PAN reagent. Compare ring to standard photographs.

No. 541 filters, washed to the 14 mm ring zone with deionized water, and dried. The ring was then sprayed with 0.35M $AgNO_3$ and exposed to ultraviolet light for ten minutes. This procedure was later modified to include a 100 µl deionized water wash applied slowly to the 33 mm ring zone prior to applications of sample to the 14 mm ring zone. This was found to be necessary because of the chloride contamination at lower levels in the filter papers, and was required to reach the maximum sensitivity of about 15 ppm for these anions.

As with the cations, black-and-white photos of the rings were taken and used in intensity comparisons. The results of these comparisons are shown in Table 106, while Table 107 gives a procedure that can be used for general scanning for anions.

### 5.2.4 Conclusions

It appears feasible to use PAN as a general scanning reagent for metals and silver nitrate-ultraviolet light as a general scan reagent for anions. Atlantic Research presently envisions using, as permanent standards for such tests, black-and-white photos similar to those previously discussed. A ring could be prepared, sprayed, and its intensity compared to those in the photos. A decision could then be made to the effect that the sample contained less than x parts Pb, y parts Cu, and so on.

Such a test procedure should serve as a rapid, simple indication of contaminated water supplies. This could be of prime importance in situations where time is of the essence. For instance, in a battlefield situation, rapid decisions as to the potability of water must be made. Any savings in time required for these decisions, such as could be attained through the use of a general scan technique, and the possible elimination of further analysis, is obviously to be desired.

## 5.3 Feasibility Studies - Ring Oven-Pesticide Analysis

### 5.3.1 Reagent Survey

In searching the literature for pesticide reagents, more emphasis

### TABLE 106. General Scan Reagents - Response of Various Anions to $AgNO_3$-UV

(Each column contains rings of equivalent concentrations)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 4 μg Cl | 4 μg $PO_4$ | 4 μg CN | 4 μg S | 2 μg S | 2 μg F | 2 μg $SO_4$ | 0.5 μg S |
| | 2 μg Cl | | 2 μg $PO_4$ | 2 μg CN | 0.5 μg CN | | 0.5 μg F |
| | | | 0.5 μg Cl | 4 μg F | | | 0.5 μg $SO_4$ |
| | | | | 0.5 μg $PO_4$ | | | |

### TABLE 107. General Scan Procedure for Anions

**33 mm attachment**

**Whatman No. 541 Filter Paper**

1. Apply 100 μl deionized water. Dry.
2. Place 14 mm attachment on ring oven.
3. Apply sample. Dry.
4. Wash to ring zone with 15 μl deionized water. Dry.
5. Spray with 0.35M silver nitrate solution. Expose to ultraviolet light for ten minutes. Compare 14 mm ring to standard photographs.

was placed on "general scan" types; for instance, those reagents which will detect organochlorines or organophosphorus compounds as a group. This seems a logical approach, as a reagent that would detect dieldrin, but no other organochlorine pesticide, would be of little use for ring oven field application. Unfortunately, few general colorimetric reagents for pesticides suitable for ring oven use were located. Those which were submitted to laboratory testing are shown in Table 108.

### 5.3.2 Arsenicals

The ring oven procedure for arsenic that appeared most suitable for the field determination of arsenical pesticides was based upon the fact that $Ag_2S$ on filter paper can be protected by arsenic sulfide from attack by concentrated HCl. Silver sulfide was deposited on the filters by bathing Whatman No. 40 paper in (1) 0.5% $AgNO_3$, (2) 5% $Na_2S'$, and (3) deionized $H_2O$. The filter was then dried. The color of the dried filter is medium brown.

The actual tests were carried out by applying 15 μl of sample to the center, washing to the 14 mm ring zone with 3M $NH_4OH$, and drying. The darkness of the paper did cause some difficulties in regular ring formation. This was corrected, however, by placing the ring oven in dimmer light, thus bringing the ring oven light into emphasis and brightening the ring annulus. After the ring was dry, it was bathed in 3:1 HCl (fresh). The background $Ag_2S$ gradually faded, leaving a dark ring zone. The first few rings prepared faded as they dried, but this fading was slowed greatly when the rings were bathed in deionized water immediately after the acid bath.

This reagent had a sensitivity of 0.1 μg arsenic, or 2 ppm arsenic based upon 50 μl samples. Gradation between 0.1 μg and a blank were reproducible with the blank showing no ring.

### 5.3.3 Organochlorines

As stated in Section 4.7 (p. 44), benzene was used as a solvent for the selected organochlorine, dieldrin. This required a reduction in

TABLE 108. Reagents for Pesticide Feasibility Studies

| Pesticide Class | Reagent | Reference |
|---|---|---|
| Arsenicals | Protective Layer Effect | 6 |
| Organochlorine | Diphenylamine-UV | 7 |
| | Rhodamine B | 8 |
| Organophosphorus | $PdCl_2-(NH_4)_2S$* | 9 |
| Cyanide | Ditrobenzene-nitrobenzaldehyde | 10 |
| | $FeCl_3$-thioacetamide | 11 |
| | $Fe(NH_4)_2(SO_4)_2$ | 11 |
| | Copper-benzidine | 11 |

*Although not examined in the laboratory, it is possible that the phosphate reagent using molybdate could prove suitable for monitoring organophosphorus pesticides by ring oven methods.

ring oven temperature (to setting No. 2) in order to insure the species of interest reached the ring zone. Both ethanol and benzene were used as washing reagents, with more success obtained when benzene served as the wash solution.

### Rhodamine B

Rhodamine B is sometimes used as a thin layer chromatographic reagent for organochlorine pesticides. It is reported to produce a purple color on a pink background in visible light with organochlorines, while the purple spot is quenched by exposure to UV light.

A ring containing 6 μg dieldrin was prepared, sprayed with a solution of 1 mg rhodamine B in ethanol and compared to a blank. No difference could be seen between the rings. When both rings were then exposed to ultraviolet light (longwave), a quenched area, in the shape of an extremely diffused ring, appeared on the filter containing the dieldrin. This ring disappeared, when it was removed from UV radiation. For this reason, it is felt that this method is not suitable for field use as the light color obtained (yellow) would extremely difficult to quantitate.

### Diphenylamine

A solution of diphenylamine in ethanol (0.015%) was prepared. Nine micrograms of dieldrin were then applied to a filter and washed to the 14 mm ring zone with benzene. Thirty microliters of diphenylamine in ethanol were applied and washed to the ring zone with ethanol. The filter was then exposed to UV light (longwave) for 10 minutes. A very faint brownish-colored ring appeared, much fainter than the amount of dieldrin present would indicate.

As the procedure called for shortwave UV (235.6 nm), an ultraviolet light with a wavelength of 254 nm was used to irradiate the ring for 10 minutes. A strong green ring appeared. Rings of lesser intensity also appeared with 3 μg and 1 μg dieldrin. One microgram dieldrin was also the sensitivity limit of the diphenylamine reagent, which is equivalent to 20 ppm dieldrin based upon 50 μl samples.

### 5.3.4 Organophosphorus Pesticides

As with the organochlorines, the organophosphorus pesticide, malathion, was dissolved in benzene in order to reach great solubility levels. Again, this necessitated a reduction in ring oven temperature to thermostat setting No. 2.

#### Palladium Chloride - Ammonium Sulfide

Various aliquots of the standard malathion solution were deposited on filters and washed to the 14 mm ring zone with 40 μl of chloroform. The ring was then dried, and sprayed with 5% aqueous palladium chloride (pH $\cong$ 2). The filter was then bathed in deionized water, followed by ammonium sulfide solution. A grey-green ring indicated the presence of malathion. A sensitivity limit of 1 μg was obtained using this method which is equivalent to 20 ppm malathion.

### 5.3.5 Cyanides

During the previous contract effort, a method for determining cyanide using dinitrobenzene-nitrobenzaldehyde reagent was evaluated (1). Although some limited success was attained at that time, it was decided during the effort which this report describes that, as the reaction was catalytic, it would not be sufficiently controllable for ring oven use. For this reason, no further evaluation was performed on dinitrobenzene-nitrobenzaldehyde. Rather, more classic techniques for cyanide analysis were examined.

#### Ferrous-Ferro Cyanide Complexes

Various attempts were made to identify cyanide ions using the tendency of cyanide to form colored complexes with both ferrous and ferric ions. Little success was attained when chemical reactions were carried out on filter paper. In solution, a blue green precipitate was formed when a solution of $Fe(NH_4)_2(SO_4)_2$ was mixed with a 1000 ppm CN solution. This precipitate, however, while it could be transferred to the ring oven, could not be washed to the ring zone.

### Thiocyanate Complexes

Another attempt to measure cyanide using the ring oven method consisted of converting the cyanide into thiocyanate by reaction with sulfide (provided by thioacetamide). The resulting thiocyanate rings were then swabbed with ferric chloride in acetone to form the dark red iron thiocyanate complex. Rings obtained from this procedure, however, showed no usable gradation.

### Copper-Benzidine

A solution consisting of a 1:1 mixture of the following components was prepared:

A: 1% benzidine acetate in 10% acetic acid

B: 1% copper(II) acetate.

Twenty microliters of this mixture were applied to a filter and washed to the ring zone (14 mm) with deionized water, then dried. The dried filter was placed over a porcelain crucible containing 100 µl standard cyanide solution and 100 µl 1M sulfuric acid. The filter was then covered with a watch glass. The ring turned blue when 1000 ppm $CN^-$ solution was used. A 100 ppm $CN^-$ solution, however, gave no discernible color change from the blank. It was obvious that this reagent was not of sufficient sensitivity. In addition, the toxicity hazards from both the benzidine and the HCN vapors eliminated this reagent's use. Therefore, no reagent for cyanides was identified which would be suitable for ring oven use.

### 5.3.6 Conclusions

The ring oven/spot test technique does not appear to be sufficiently senstitive for monitoring pesticides in water at the limits shown in Table 17 (p. 45) for long-term consumption. Extraction procedures, however, for concentration of the pesticides prior to ring oven analysis should greatly improve the sensitivity obtained.

Reagents were found for three of the four classes of pesticides: organochlorines, diphenylamine-UV; organophosphorus, palladium chloride-ammonium sulfide; and arsenicals, protective layer effect. The first two

**reagents for organochlorines and organophosphorus are not specific for the pesticides only, according to the literature. They are functional group reagents; that is, they react with only a portion of the molecule. It would seem that this would have to be the case, as in order to react with a broad spectrum of pesticides within a class, a reagent would have to be functional-group sensitive. Thus, any time the functional group was encountered, whether in a pesticide or in a nontoxic compound of similar structure, a positive reaction would be encountered.**

**The ring oven method should prove suitable, however, as a screening method for highly contaminated waters such as might result from deliberate sabotage. With a concentration step prior to ring oven analysis, greater sensitivities should be attainable.**

# 6.0 CONCLUSIONS AND RECOMMENDATIONS

## 6.1 Statistical Evaluation

The results, conclusions, and recommendations for the statistical evaluation for the ring oven procedures for copper, calcium, zinc, magnesium, iron, lead, sulfate, chloride, fluoride and nitrate are summarized in Table 109. These conclusions are discussed in the following paragraphs.

### 6.1.1 Fractional Factorial Tests

Several conclusions may be drawn from the data and results of the analysis of the fractional factorial tests:

a) It is quite clear that both reagent age and reagent temperature have significant results. In a kit situation, any effect due to reagent age can be eliminated by requiring reagents to be prepared fresh at the time of use. This should be easily accomplished through the use of pre-packaged reagents. Effects due to reagent temperature require the use of reagents at ambient temperatures.

b) In general, the results at the high ion concentration are considerably less accurate than the results at the low ion concentration. The results have both greater bias and greater dispersion. This is probably due to the fact that the eye has more difficulty in distinguishing color intensity differences at higher concentrations. A small change in ring intensity is less noticeable at higher concentrations, so results are less accurate. In most cases, however, ring oven procedures are capable of functioning well for general screening at high ion concentrations as long as the concentrations are in the "linear portion" of the curve of color intensity versus ion concentration. This proves to be the case for the procedures for the ions copper, magnesium and zinc, since all three procedures should be useful for general screening at concentrations above those tested under this contract. Calcium, chloride

TABLE 109. Summary of Statistical Evaluation

| Ion | Fractional Factorial Tests | Qualifications Tests | Comments |
|---|---|---|---|
| Copper | Effects due to ion concentration and to interaction between color and reagent temperature. | Able to place samples on correct side of decision level with great success. | Even though there is a highly significant effect due to ion concentration, this can be compensated for by multiple measurements. The highly significant interaction between color and reagent temperature (40°C) is lessened by utilizing reagents at nominal ambient temperatures. |
| Zinc | Effects due to reagent temperature, reagent age, ion concentration, and interactions between color and reagent age; reagent age and reagent temperature; reagent temperature and reagent concentration; and reagent age and ion concentration. | Able to place samples on the correct side of the decision concentration on an average of 86% of the time. | Reagent age effects may be compensated for in kit by preparing fresh reagent at time of use from sealed packets and bottles. Multiple analysis of the small number of samples required in a given field situation should increase accuracy and precision and lessen effects due to ion concentration. |
| Magnesium | Effects due to reagent temperature, reagent age, ion concentration, and interaction between reagent age and ion concentration. | High results at lower ion concentration, although samples are still placed on correct side of decision level in most cases. | In kit situation, reagents should be prepared fresh at time of use from sealed packets and bottles. Multiple measurements on each sample should be made in the field to lessen effects due to ion concentration. |
| Calcium | Effects due to reagent age and ion concentration. | Less accurate at areas outside the standard range, but still able to place samples on correct side of the decision level in most cases when sample concentration exceeds decision concentration. | Reagents must be prepared fresh at time of use from sealed packets and bottles in field situation. In addition, more measurements should be made in field on individual samples. At sample concentrations above the decision concentration, smaller sample sizes should be used. |

TABLE 109. (Continued)

| Ion | Fractional Factorial Tests | Qualifications Tests | Comments |
|---|---|---|---|
| **Iron** | Erratic results due to high iron backgrounds in filter papers, reagents. This led to cessation of further tests. | Not conducted. | Test should still be useful in kit situation for general screening purposes at concentrations above 1 ppm iron. Present limit of 0.3 ppm is only an aesthetic maximum. |
| **Lead** | Erratic results due to extreme sensitivity of reagent to contaminants in reagents, filter papers, etc. This led to cessation of further tests. | Not conducted. | Extreme sensitivity of reagent is advantage; no kit on the market can detect lead at 0.05 ppm. Difficulty in isolating lead from contaminants, however, makes it doubtful that this test can be adapted for kit use. |
| **Chloride** | Effect due to ion concentration | Test less reliable at area near decision concentration. | Before any kit use, suggest broadening the standard range. |
| **Sulfate** | No significant effects. | Less reliable immediately above decision level. | More measurements on individual samples in field situation should improve reliability. |
| **Fluoride** | Effect due to ion concentration. | Very erratic results on both natural water samples and blanks. | Test is apparently sensitive to factors such as pH; fluoride test not suitable for ring oven use at this time. |
| **Nitrate** | Erratic results due to variance in operator technique and filter paper contamination.<br>Further testing suspended. | Not conducted. | Nitrate test appears to be unsuitable for field use unless operator can prepare his own standard rings. |

and sulfate, on the other hand, were all evaluated near the saturation points of their respective reagents; that is, on the non-linear portion of the color intensity-concentration curves. If necessary, this can be compensated for by use of smaller sample sizes.

c) Various other factors and interactions of factors are determined to be significant for different ions as discussed below. Several methods to eliminate significant factors which can be utilized in a field test kit are feasible. Turbidity, for example, will not be a problem, as the Army has stated that any water utilized in the field for drinking purposes will be filtered prior to use. The effect of reagent age can be minimized if reagents are packaged as solids and mixed with solvent in the field immediately before use. This packaging method, which was used because of short shelf life for the sulfate reagent, eliminated the age of the reagent as a significant factor. The ion effect can also be minimized if the ring oven is used as a general screening tool for simple "go-no go" decisions, as discussed in Section 4.4.4 (p. 38). In the case for all factors, it must be recognized that the factors used were at their extreme values, which will seldom occur in a field situation.

For copper there is a highly significant interaction between color and turbidity. Zinc showed highly significant effects for detection reagent temperature, reagent age, and for the interactions between color-reagent age, reagent temperature-reagent age, reagent temperature-ion concentration, and reagent age-ion concentration. The magnesium test showed highly significant effects for the interaction between reagent age and ion concentration. For calcium, reagent age and ion concentration showed only a significant effect. Iron showed a highly signficant effect due to ion concentration, as did lead.

For chlorides, a high significant effect was seen from interaction between reagent age and chlorine concentration. Sulfate showed no highly significant effects. Fluoride showed only the ion concentration as a highly significant effect, while nitrate showed all three of the generally significant effects, i.e., reagent age, reagent temperature, and ion concentration.

### 6.1.2 Qualifications Tests

The results of the qualifications tests demonstrated that the ring oven procedures for six of the ten ions (copper, calcium, zinc, magnesium sulfate, and chloride) are feasible as general screening methods for these ions in water. However, in developing a field test kit using these procedures, the developer must be careful to select the proper color standards. As tolerances are reduced (i.e., greater sensitivity is required) these methods may become unacceptable for field use. Thus acceptability of the ring oven methods for water analysis will depend upon the user's required precision tolerance at the concentrations where a decision has to be made concerning acceptability of the water being tested.

The copper test showed average errors of 0.003 ppm at the 0.4 ppm Cu level, 0.16 ppm at the 0.7 level, 0.05 ppm at the 1.5 ppm level and 0.15 ppm at the 3 ppm level. The precision obtained for the copper method was better than that obtained during the ruggedness tests, while at the same time, a small operator variability was obtained. During the general screening analysis, 100% of all samples above the decision level were correctly placed as being unacceptable for drinking purposes.

For zinc, the magnitude of the operator effect was considerably less than the variability of repeated measurements by the same operator. However, when an operator analyzes a large number of samples consecutiviely for the same ion, the number of repetitive actions can lead to loss of concentration by the operator. This can cause errors which would not occur in the field, where only one or two samples would be analyzed at a time. In that situation, an operator would know if two measurements on a single sample were not sufficiently reproducible. In this case, the operator should simply make more measurements. The average errors for the four zinc ion levels were 0.6 ppm, 1.0 ppm, -0.07 ppm and -1.2ppm for 1, 3, 7 and 9 ppm zinc,respectively. At levels above the decision concentration, correct decisions as to water potability were made 56 out of 60 times.

The magnesium test appeared to give high results at both the 40 ppm and 400 ppm Mg levels. This was found to be due, however, not to the test itself, but to a sample effect, i.e., the presence of a magnesium-containing organism or precipitate in various magnesium solutions. In spite of this problem, the magnesium ring oven method functioned well as a general screening tool for natural waters, making the correct "go-no go" decision for samples above the decision concentration 55 out of 60 times. In addition, a greater precision was found in the magnesium qualifications tests than in this ion's ruggedness tests.

The calcium ion's qualifications tests showed a highly significant factor for the different ion levels, which was probably due to the high readings at the 600 ppm level. As this level was far outside the permanent standard values, this was not unexpected. A precision similar to that obtained for calcium during the ruggedness tests was found, while the operator effect for this ion was estimated as zero. The average errors for the different ion levels were on the whole good, with the only problem being encountered at a level above the highest valued permanent standard as discussed above. In addition, as a general scan test, the method placed 55 out of 60 samples with levels of Ca which would be unacceptable on the correct side of the decision level.

As a rule, the chloride test functioned at all values except at the 700 ppm value. This appeared to be due to the fact that this level was too close to the standard value of 600 ppm Cl for sufficient color intensity differentiation. In fact, the standard increments themselves should be broadened in a field test kit, as the dark rings obtained tend to make differentiation more difficult. This is demonstrated by the fact that a significant effect was obtained due to operator, ion value, and their interaction. Even with the present standards, however, a 77% value was obtained for the number of correct "go-no go" decisions at the value farthest above the decision concentration.

A similar effect due to dark rings and the difficulty in reading them was found for the sulfate test, although to a lesser degree. Again, the 600 ppm test level was too close to the 400 ppm and 1000 ppm standard levels to always allow for sufficient gradation, resulting in a significant interaction between ion level and operator variability, as well as ion level and water sample. Still, at levels above the decision level, over 80% of the samples were correctly found to be unacceptable for drinking purposes. Average errors for all four levels did not exceed 112 ppm $SO_4$, which is excellent considering the range covered by the standards.

Four ions were deemed to be unacceptable at the present time for inclusion in a kit. These ions were fluoride, nitrate, iron and lead. Two of these ions, iron and lead, were subjected to only limited statistical evaluation, as the ring oven technique did not appear to perform satisfactorily at the lower concentration ranges of these ions. Ring oven techniques, however, should still prove feasible for these ions, particularly iron, if decision concentration limits can be increased and if clean-up procedures for reagents and filters can be developed. This alternative would appear viable if short-term human consumption is considered, as the present iron limit is an aesthetic, rather than a medical, maximum.

In the case of fluoride, both fractional factorial and qualifications tests were performed. Fractional factorial tests were satisfactory, but erratic results were obtained during the qualifications tests. Time was not available to locate the cause of these erratic results; however, the fractional factorial test data would seem to suggest that the fluoride test is better than that indicated by the qualifications test results. The problems encountered should be resolved, particularly since a permanent standard set was prepared for fluoride. The fluoride test, however, is not suitable for incorporation into a kit at this time.

The nitrate method was subjected to fractional factorial tests only, although permanent standards were also prepared for this ion. Problems were encountered during the latter part of this contract effort with randomly contaminated filter papers. In addition, the technique itself appears to be highly operator sensitive, with the best results obtained when the ring oven operator prepared his or her own standards. Obviously, this alternative is not viable for field use at the present time.

Although operators tended to report numbers at or near those of the standards used, this did not appear to be the result of a bias toward the standard values. Rather, it was due to narrowness of the standard ranges, which were minimized prior to statistical testing. These rings thus showed subtle color gradations which were considered to be the minimum observable. The samples themselves were then prepared so that their concentrations fell between the standard range values. Thus, an operator might have to differentiate a 0.5 ppm concentration gradient while analyzing a sample, when a 1 ppm concentration gradient had been determined to produce the minimum color gradation that the eye could distinguish.

For example, assume a sample contained 1.5 ppm cooper. It was established that it was possible for an operator to distinguish between 1 ppm and 2 ppm copper rings. An operator might well report the sample as containing 2 ppm copper, rather than 1.5 or 1.7 ppm. Therefore, while the data suggests a bias toward the standards, it is due primarily to narrowness of the standard range.

Hardware for field use should be evaluated in greater detail. This includes adaptation of the ring oven for battery power, definition of quality control standards for reagents, filters, etc., and investigation of suitable packaging methods such as metered aerosols. Toxicity tests should be performed on those reagents for which this information is not available. Appendix D lists the contents of a possible ring oven field test kit.

The ring oven also appears to offer many advantages over water test kits currently on the market, including durability, ease of operation (operators of widely varying educational and technical backgrounds were able to use the ring oven skillfully), and low cost, as well as offering comparable reliability as a screening tool.

### 6.2 General Scan Reagents

General scan reagents were located for both anions and cations. Silver nitrate-ultraviolet light gave positive reactions with the ions chloride, phosphate, cyanide, sulfide, fluoride, and sulfate. PAN reagent was found to react with the cations iron, cadmium, lead, zinc and copper. It is recommended that further work be performed on analysis of actual multi-ion samples using these techniques, and that further investigation of black-and-white photography as a method of preparing permanent standards be performed.

## 6.3 Pesticide Feasibility Studies

Reagents were located for three of the four pesticide classes: organochlorines, organophosphorus, and arsenicals. Although sensitivities did not reach the limits for long term consumption, it is probable that the ring oven can be used as a scanning device to detect gross pesticide contamination of water supplies, such as might occur in the case of sabotage. Work required to further define this possibility includes sample analyses and statistical evaluation of the results.

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# APPENDIX A

# DEVELOPMENT OF RING OVEN PROCEDURES

# APPENDIX A

## DEVELOPMENT OF RING OVEN PROCEDURES

This Appendix describes the development of ring oven procedures for the ten ions that were statistically evaluated during the present contract period. This development work was performed under Army Contract No. DADA17-73-C-3112.

### I. RING OVEN PROCEDURE

The separation of compounds contained in a sample into one or more groups is a critical first step in chemical analysis. The separation steps must be selected in such a way that components of one group do not interfere with the subsequent identification of each component of another group. By choosing the proper separation scheme, interferences normally associated with a particular analytical test can be largely eliminated. Conventional separation techniques are not suitable for use in analytical methods involving trace components in small samples. The ring oven, however, is ideally suited for this application since it is designed to handle small quantities of sample.

Separations are effected on the ring oven by placing a small amount (1 to 2 drops) of the sample in the center of a circular filter paper, adding a suitable reagent to localize one or more components as a precipitate on the paper, and eluting the remaining components to the outer zone of the filter paper with a solvent (wash reagent) by means of the capillary action of the test paper. At the outer zone, the hot aluminum block vaporizes the solvent, leaving a concentrated, sharply defined "ring" of materials. The ring can then be divided into sectors, and selective spot tests may be used to analyze for suspected ions. The center portion where some components are localized (disk) may then be eluted onto another filter paper, and the procedure repeated as often as needed to effect the degree of separation desired. The entire process is very rapid, requiring as little as two minutes for a two-component system. The ring oven procedure is diagrammed in Figure A-1.

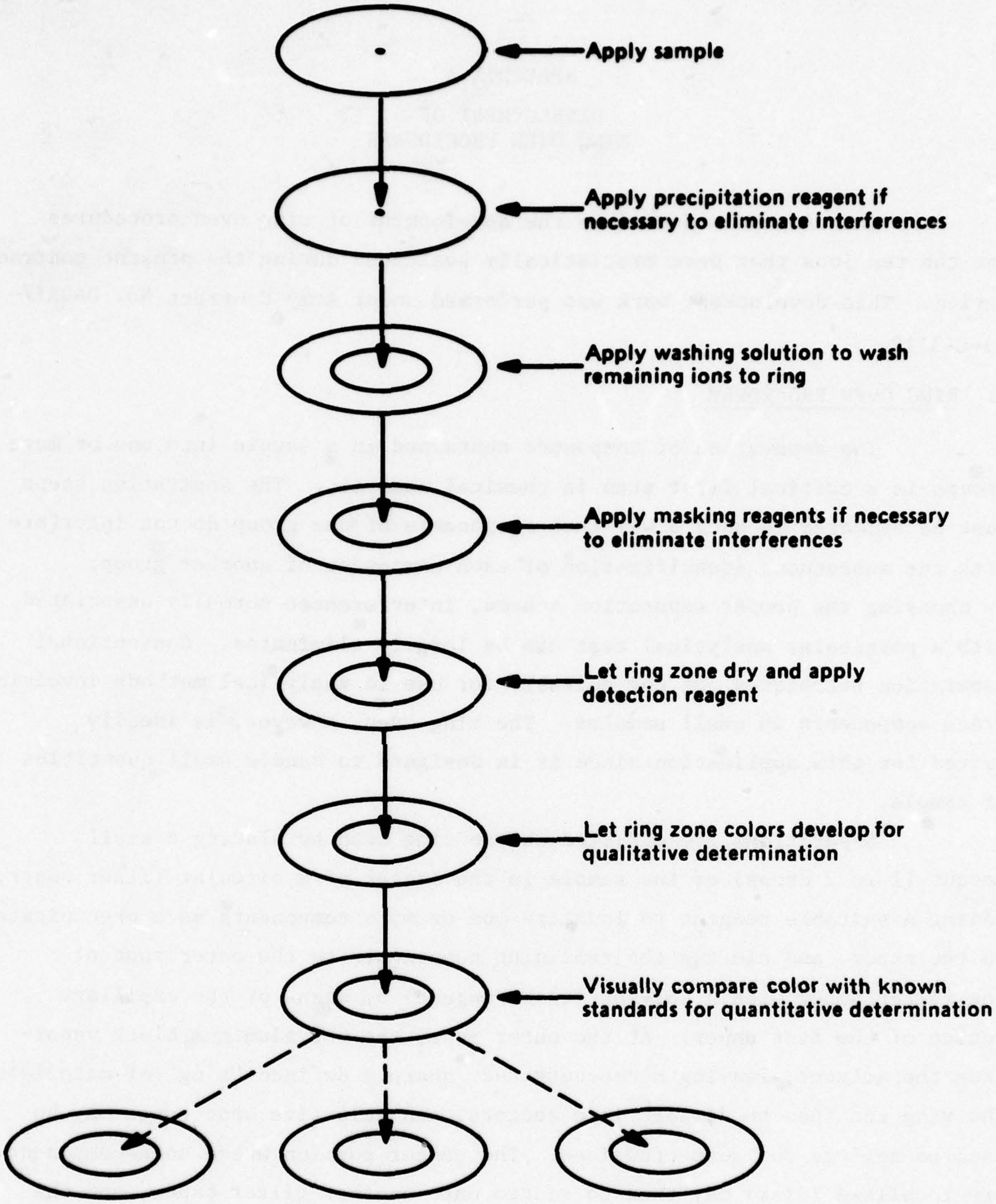

Figure A-1. Ring Oven Procedure

## II. DETECTION REAGENT EVALUATION

Detection reagents for ring oven testing were evaluated according to several criteria. After a thorough search of the literature for colorimetric reagents, selection of those reagents suitable for laboratory ring oven evaluation was made. Some of the criteria considered were sensitivity, selectivity, simplicity, availability, and shelf-life.

Each trial reagent was first tested on the ring oven with the cation or anion standard solution that it was supposed to detect. (See Tables A-1 and A-2). This determined what a positive test should entail. Reagents were then tested through the entire concentration range of interest using standard solutions until a lower limit was reached, or until the minimum concentration was reached, whichever occurred first. A blank standard was also run to determine what response the reagent would give when the detectable ion was not present. Reagents were generally graded as to their ability to measure gradual cation or anion concentration changes by corresponding color intensity differences and by ability to cover the entire range of interest. The detection reagents selected for each ion are given in Table A-3.

## III. INTERFERENCE EVALUATION - SEPARATION SCHEME DEVELOPMENT

After determining that a candidate detection reagent was sufficiently sensitive, the next step was to determine the specificity of the reagent. This was accomplished by testing the reagent's reaction to various species commonly found in natural waters.

When interferences were identified, a suitable separation scheme was developed in order to prevent the interfering species from reaching the ring zone. Some of the separation methods utilized were precipitation techniques, masking techniques, and ion exchange. An example of one of these schemes, for the separation of copper from iron, is shown in Figure A-2.

## TABLE A-1. CONCENTRATION RANGE OF VARIOUS CATION STANDARDS

| Cation | Range | Solutions Prepared | μg/μl Sample |
|---|---|---|---|
| Fe | 0.1-10 ppm | 10 ppm | .01 μg |
| | | 1 ppm | .001 μg |
| | | 0.1 ppm | .0001 μg |
| Mg | 10-5000 ppm | 5000 ppm | 5 μg |
| | | 2500 ppm | 2.5 μg |
| | | 1000 ppm | 1.7 μg |
| | | 500 ppm | .5 μg |
| | | 100 ppm | .1 μg |
| | | 10 ppm | .01 μg |
| Pb | 0.05-1.0 ppm | 1.0 ppm | .001 μg |
| | | 0.5 ppm | .0005 μg |
| | | 0.1 ppm | .0001 μg |
| | | 0.05 ppm | .00005 μg |
| Zn | 1 - 20 ppm | 20 ppm | .02 μg |
| | | 10 ppm | .01 μg |
| | | 5 ppm | .005 μg |
| | | 1 ppm | .001 μg |
| Cd | 0.01 - 0.1 ppm | 0.1 ppm | .0001 μg |
| | | 0.05 ppm | .00005 μg |
| | | 0.01 ppm | .00001 μg |
| Cr | 0.01 - 1 ppm | 1.0 ppm | .001 μg |
| | | 0.5 ppm | .0005 μg |
| | | 0.1 ppm | .0001 μg |
| | | 0.05 ppm | .00005 μg |
| | | 0.01 ppm | .00001 μg |

## TABLE A-2. (Continued)

| Cation | Range | Solutions Prepared | µg/µl Sample |
|---|---|---|---|
| Cu | 0.1 - 5 ppm | 5.0 ppm | .005 µg |
| | | 2.5 ppm | .0025 µg |
| | | 1.0 ppm | .001 µg |
| | | 0.5 ppm | .0005 µg |
| | | 0.1 ppm | .0001 µg |
| Ca | 20 - 10,000 ppm | 10,000 ppm | 10.0 µg |
| | | 5,000 ppm | 5.0 µg |
| | | 1,000 ppm | 1.0 µg |
| | | 500 ppm | .5 µg |
| | | 100 ppm | .1 µg |
| | | 20 ppm | .02 µg |
| Mn | 0.02 - 2 ppm | 2 ppm | .002 µg |
| | | 1 ppm | .001 µg |
| | | 0.1 ppm | .0001 µg |
| | | 0.02 ppm | .00002 µg |

## TABLE A-2. CONCENTRATION RANGE OF VARIOUS ANION STANDARDS

| Anion | Range | Solutions Prepared | µg/µl Sample |
|---|---|---|---|
| $Cl^-$ | 10 - 20,000 ppm | 20,000 ppm | 20 µg |
| | | 10,000 ppm | 10 µg |
| | | 5,000 ppm | 5 µg |
| | | 2,500 ppm | 2.5 µg |
| | | 1,000 ppm | 1 µg |
| | | 500 ppm | 0.5 µg |
| | | 100 ppm | 0.1 µg |
| | | 10 ppm | 0.01 µg |
| $F^-$ | 0.1 - 10 ppm | 10 ppm | 0.01 µg |
| | | 1 ppm | 0.001 µg |
| | | 0.1 ppm | 0.0001 µg |
| | | ... | |
| | | 0.1 | |
| $SO_4^=$ | 10 - 3000 ppm | 3,000 ppm | 3 µg |
| | | 2,000 ppm | 2 µg |
| | | 1,000 ppm | 1 µg |
| | | 500 ppm | 0.5 µg |
| | | 100 ppm | 0.1 µg |
| | | 10 ppm | 0.01 µg |
| $NO_3^-$ | 1 - 20 ppm | 20 ppm | 0.02 µg |
| | | 10 ppm | 0.01 µg |
| | | 5 ppm | 0.005 µg |
| | | 1 ppm | 0.001 µg |
| $CN^-$ | 0.1 - 5 ppm | 5 ppm | .005 µg |
| | | 2.5 ppm | .0025 µg |
| | | 1.0 ppm | .001 µg |
| | | .5 ppm | .0005 µg |
| | | .1 ppm | .0001 µg |
| $PO_4^\equiv$ | .02 - 2 ppm | 2 ppm | .002 µg |
| | | 1 ppm | .001 µg |
| | | .5 ppm | .0005 µg |
| | | .1 ppm | .0001 µg |
| | | .02 ppm | .00002 µg |

TABLE A-3. Reagents Selected for Ring Oven Use

| Ion | Reagent |
|---|---|
| Copper | Dithiooxamide |
| Iron | Ferrozine |
| Lead | Thiazolylazonaphthol |
| Zinc | Pyridyl-azo-naphthol |
| Magnesium | p-nitrobenzene-azoresorcinol |
| Calcium | Glyoxal bis(hydroxyanil) |
| Manganese | Periodate/tetrabase |
| Cadmium | Diphenylcarbazide |
| Nitrate | Diphenylbenzidine |
| Fluoride | Thorium chloranilate |
| Chloride | Silver nitrate-ultraviolet light |
| Sulfate | Barium chloride-rhodizonate |
| Phosphate | Molybdate-ascorbic acid |
| Cyanide | Nitrobenzaldehyde-dinitrobenzene |
| Chromium | Periodate-tetrabase |

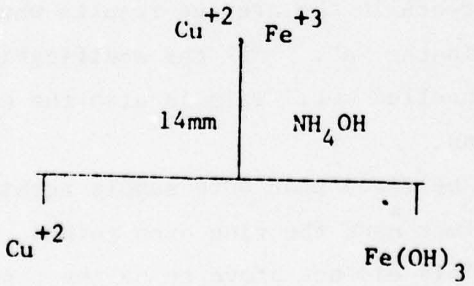

Figure A-2. Copper Separation Scheme

## IV. PRELIMINARY RUGGEDNESS AND QUALIFICATIONS TESTING

During the second year's effort on Contract No. DADA17-73-C-3112, those eight ions for which procedures had been developed during the first year's effort (iron, zinc, lead, magnesium, chloride, fluoride, nitrate and sulfate) were subjected to preliminary ruggedness and qualifications testing in order to determine their suitability for further evaluation.

The ruggedness testing was designed in order to show the effects of gross changes in various factors that are present in the natural water environment or in preparation and handling of samples and reagents. These factors were reagent concentration, reagent temperature, wash solution pH, sample temperature, sample pH, sample color, and sample turbidity.

The sample matrix used for this ruggedness testing is based upon one designed by Youden[1]. Table A-4 shows the basic matrix. Two levels for each of the variables were selected from those given for the Preventive Medicine Kit.

This test allows the effects of the seven variables to be determined by the unique design of the experiments. Referring to Table A-4, it can be seen that each value of every condition appears four (4) times. Further observation shows that when, for example, condition 1 is "A", all the other conditions exist in the capital and small letter states an equal number of times. This is also true when condition 1 is in the "a" state. Thus, the effect of a modification of condition 1 (State "A" to State "a") is found by the difference in the average results when it is in the "A" state and when it is in the "a". All the modifications due to the other six conditions are cancelled out. This is also the case for the remaining experimental conditions.

It had been believed that both sample turbidity and color would have a detrimental effect upon the ring oven method, through dampening of the color produced. This did not prove to be the case, Preliminary

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[1] Youden, W. J., "Statistical Techniques for Collaborative Tests," AOAC Publication, 1973.

TABLE A-4. Design for the Experimental Conditions

| Experimental Condition | Values of Conditions for Determination No. 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| 1 | A | A | A | A | a | a | a | a |
| 2 | B | B | b | b | B | B | b | b |
| 3 | C | c | C | c | C | c | C | c |
| 4 | D | D | d | d | d | d | D | D |
| 5 | E | e | E | e | e | E | e | E |
| 6 | F | f | f | F | F | f | f | F |
| 7 | G | g | g | G | g | G | G | g |
| Observed results | s | t | u | v | w | x | y | z |

List of Conditions to be Studied and Their Altered and Assigned Values

| Condition | No. | Letter | Value for Capital Letter | Value for Small Letter |
|---|---|---|---|---|
| Sample pH | 1 | A,a | 7 | 5,9 |
| *Sample color (true units) | 2 | B,b | 0 | 10,200 |
| *Sample turbidity (JTU) | 3 | C,c | 0 | 0.1,5.0 |
| Detection reagent concentration | 4 | D,d | D** | d',d** |
| Wash solution pH | 5 | E,e | E** | e',e** |
| Temperature of Sample °C | 6 | F,f | 25 | 10, 40 |
| Temperature of detection reagent °C | 7 | G,g | 25 | 10, 40 |

* Color and turbidity standards were made up and analyzed according to procedures outlined in "Standard Methods for the Examination of Water and Wastewater."

** The range of these parameters depended on which detection reagent was used and which ion was examined and thus, no general range applied for all detection reagents or all wash solutions. Each of these parameters were examined based upon the extremes for individual procedures.

experiments using color and turbidity solutions greatly in excess of the upper limits (2.5 and 60 times, respectively), showed only minimal effects. This non-effect was later confirmed in the ruggedness tests.

Some preliminary qualifications testing was also performed. Natural water samples that had already been analyzed by standard methods were obtained from the Army Environmental Hygiene Agency and from the Environmental Protection Agency's Wheeling, West Virginia, laboratory. Analyses and color decisions were performed by relatively untrained personnel using standard rings prepared according to the procedures utilized for sample analysis.

The results obtained for the zinc analysis along with the values of the sample rings used, are shown in Table A-5. Results obtained by Atlantic Research Corporation and by the U. S. Army Medical Research and Development Command were generally in good agreement, and when low results were obtained by Atlantic Research, as in the case of sample B-228, this was found to be due to over-application of the reagent, which can be easily corrected. Similarly, good agreement between ring oven and standard methods was obtained for the other seven ions.

## V. CONCLUSIONS

Ring oven/spot test procedures were shown to be feasible for the analysis of selected ions found in natural water sources. This feasibility was demonstrated by using ring oven procedures to successfully analyze actual water samples. In addition, it was shown that ring oven separation techniques coupled with spot test procedures, could be used by relatively untrained personnel.

It was decided to evaluate more critically the procedures for the original eight ions, along with those of the second ion group, which seemed most promising (copper and calcium). This would be accomplished through multi-operator analysis of a great number of water samples at various ion levels, followed by intensive statistical analysis of the results. The main body of this report gives a description of this evaluation.

TABLE A-5. Zinc Results
Range: 1 - 20 ppm

| Sample No. | ARC | AMRDC | Sample No. | ARC | AMRDC | Sample No. | ARC | AMRDC |
|---|---|---|---|---|---|---|---|---|
| B-123 | <1 | 0.36 | D-252 | <1 | 0.04 | F-178 | <1 | 0.19 |
| B-125 | <1 | 0.06 | D-253 | <1 | 0.07 | F-179 | <1 | 0.42 |
| B-126 | <1 | 0.06 | D-255 | <1 | 0.03 | F-180 | <1 | 0.09 |
| B-127 | <1 | 0.04 | D-256 | <1 | 0.04 | F-181 | <1 | 0.04 |
| B-128 | <1 | 0.12 | D-257 | <1 | 0.05 | F-182 | <1 | 0.08 |
| B-129 | <1 | 0.03 | D-258 | <1 | 0.03 | F-183 | <1 | 0.05 |
| D-129 | <1 | 0.07 | D-259 | <1 | 0.07 | F-184 | <1 | 0.07 |
| B-131 | <1 | 0.21 | D-260 | <1 | 0.12 | F-185 | <1 | 0.34 |
| B-132 | <1 | 0.03 | D-261 | <1 | 0.14 | F-186 | <1 | 0.73 |
| B-133 | <1 | 0.06 | D-262 | <1 | 0.03 | F-187 | <1 | 0.12 |
| B-134 | <1 | 0.03 | D-263 | <1 | 0.02 | F-188 | <1 | 0.03 |
| B-135 | <1 | 0.02 | D-265 | <1 | 0.04 | F-189 | <1 | 0.14 |
| B-136 | <1 | 0.04 | D-266 | <1 | 0.03 | *F-266 | <1 | 0.47 |
| B-137 | <1 | 0.04 | D-267 | <1 | 0.08 | B-124 | 1 | 0.17 |
| B-138 | <1 | 0.21 | D-268 | <1 | 0.31 | B-130 | 1 | 0.41 |
| B-139 | <1 | 0.70 | D-270 | <1 | 0.02 | B-154 | 1 | 3.4 |
| B-140 | <1 | 0.03 | D-271 | <1 | 0.03 | *B-200 | 1 | 3.570 |
| B-141 | <1 | 0.08 | D-272 | <1 | 0.03 | *B-206 | 1 | 1.250 |
| B-142 | <1 | 4.3 | D-273 | <1 | 0.16 | *B-210 | 1 | 3.970 |
| B-143 | <1 | 0.33 | D-274 | <1 | 0.04 | *B-215 | 1 | 3.800 |
| B-144 | <1 | 0.52 | D-275 | <1 | 0.08 | *B-216 | 1 | 1.510 |
| B-145 | <1 | 0.42 | D-276 | <1 | 0.06 | D-278 | 1 | 0.60 |
| B-146 | <1 | 0.10 | F-167 | <1 | 0.24 | *D-345 | 1 | 1.805 |
| B-147 | <1 | 0.06 | F-168 | <1 | 0.91 | D-264 | 2 | 2.1 |
| B-148 | <1 | 0.24 | F-169 | <1 | 0.04 | *B-228 | 2 | 7.150 |
| B-149 | <1 | 0.17 | F-170 | <1 | 0.06 | *B-232 | 2 | 1.040 |
| B-150 | <1 | 0.07 | F-172 | <1 | 0.03 | *B-190 | 3 | 3.880 |
| B-151 | <1 | 0.75 | F-173 | <1 | 0.05 | *B-195 | 3 | 3.610 |
| B-152 | <1 | 0.02 | F-175 | <1 | 0.26 | *B-202 | 3 | 4.470 |
| B-153 | <1 | 0.27 | F-176 | <1 | 0.85 | *A-325 | 4 | 3.680 |
| B-155 | <1 | 0.09 | F-177 | <1 | 0.27 | *B-192 | 4 | 2.980 |
|  |  |  |  |  |  | *B-194 | 5 | 8.375 |
|  |  |  |  |  |  | F-174 | 8 | 5.4 |

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*From second group of samples

# APPENDIX B

# STATISTICAL ANALYSIS OF THE EFFECT OF OMITTING COLOR AT HIGH CHLORINE LEVEL IN FRACTIONAL FACTORIAL TESTS

# APPENDIX B

## STATISTICAL ANALYSIS OF THE EFFECT OF OMITTING COLOR AT HIGH CHLORINE LEVEL IN FRACTIONAL FACTORIAL TESTS

For the fractional factorial test data analyzed in this report, the factor color was omitted at the high chlorine level. The data was analyzed as the factor color was present at both chlorine levels. To see the effect of this we considered, for simplicity of notation, an experiment in which there are only four factors, each at two levels. These are:

A = chlorine
B = ion level
C = color
D = factor D.

For the low chlorine level (level 1) the model is:

$$Y_{1jk} = \mu + \alpha_1^A + \alpha_j^B = \alpha_k^C + \alpha_\ell^D + \alpha_{1j}^{AB} + \alpha_{1\ell}^{AD} + \alpha_{jk}^{BC} + \alpha_{j\ell}^{BD} + \alpha_{k\ell}^{CD} + \varepsilon_{1jk\ell}{*}$$

For the high chlorine level (level 2) the model is:

$$Y_{2jk\ell} = \mu + \alpha_2^A + \alpha_j^B + \alpha_\ell^D + \alpha_{2j}^{AB} + \alpha_{2\ell}^{AD} + \alpha_{j\ell}^{BD} + \varepsilon_{2jk\ell}$$

The models are subject to the usual constraints: the sum of any $\alpha$ over any index which appears is zero, e.g., $\alpha_1^A + \alpha_2^A = 0$, $\alpha_{11}^{AB} + \alpha_{12}^{AB} = 0$, etc.

In the calculations below, when a dot (·) replaces a subscript, this indicates summation over that subscript. If a bar is also placed over the Y, this indicates the average. Thus, $\bar{Y}_{1\cdots} = \sum_j \sum_k \sum_\ell Y_{1\cdots}/8$.

### Main Effects

For any main effect, the SS is calculated as the squared difference between the corresponding means multiplied by 8, e.g.,

---

* All indices (j, k, 1) take on the values 1 or 2.

$$SSA = 8(\bar{Y}_{1\cdots} - \bar{Y}_{2\cdots})^2 = [(Y_{1\cdots} - Y_{2\cdots})^2/32]$$

(Note that in SSA the 8 and 32 are appropriate for the original experiment which had 32 observations, not for this reduced experiment). Thus, if $\bar{Y}_{1\cdots} - \bar{Y}_{2\cdots}$ involves only $\alpha_1^A$ and $\alpha_a^A$ and $\varepsilon$ terms, the F test using SSA is appropriate for testing whether there is a significant effect due to factor A.

Ignoring the $\varepsilon$ terms, we have (using the constraints on the model)

$$\bar{Y}_{1\cdots} = \mu + \alpha_1^A$$

$$\bar{Y}_{2\cdots} = \mu + \alpha_2^A$$

and $$Y_{1\cdots} - \bar{Y}_{2\cdots} = \alpha_1^A - \alpha_2^A$$

and the resulting F test is perfectly valid.

For the other factors it becomes a bit more complicated. For SSB we need $\bar{Y}_{\cdot 1\cdot\cdot} - \bar{Y}_{\cdot 2\cdot\cdot}$

$$\bar{Y}_{\cdot j\cdot\cdot} = (\bar{Y}_{1j\cdot\cdot} + \bar{Y}_{2j\cdot\cdot})/2$$

$$\bar{Y}_{1j\cdot\cdot} = \mu + \alpha_1^A + \alpha_j^B + \alpha_{1j}^{AB}$$

$$\bar{Y}_{2j\cdot\cdot} = \mu + \alpha_2^A + \alpha_j^B + \alpha_{2j}^{AB}$$

thus $$\bar{Y}_{\cdot j\cdot\cdot} = \mu + \alpha_j^B$$

and $$\bar{Y}_{\cdot 1\cdot\cdot} - \bar{Y}_{\cdot 2\cdot\cdot} = \alpha_1^B - \alpha_2$$

and the resulting F test is perfectly valid and is not affected by the absence of color at the high chlorine level.

For SSC we need $\bar{Y}_{\cdot\cdot 1\cdot} - \bar{Y}_{\cdot\cdot 2\cdot}$

$$\bar{Y}_{..j.} = (\bar{Y}_{1.j.} + \bar{Y}_{2j..})/2$$

$$\bar{Y}_{1.j.} = \mu + \alpha_1^A + \alpha_j^C$$

$$\bar{Y}_{2.j.} = \mu + \alpha_2^A$$

$$\bar{Y}_{..j.} = \mu + \alpha_1^C/2$$

and $$\bar{Y}_{..1.} - \bar{Y}_{..2.} = (\alpha_1^C - \alpha_2^C)/2$$

and while the test remains perfectly valid, the power (sensitivity) of the test will be decreased.

A similar calculation shows that for factor D, the test is not affected.

**Interactions**

For testing interactions, the calculations are similar.

1. For interactions where neither factor is color, the F test is not affected, e.g.,

$$\text{SSAB} = 2(\bar{Y}_{11..} + \bar{Y}_{22..} - \bar{Y}_{12..} - \bar{Y}_{21..})^2$$

(Again note that the 2 is the appropriate multiplier for our 6 factor half replicate, not for this reduced model). The result of calculating separately the various means will give:

$$\bar{Y}_{11..} + \bar{Y}_{22..} - \bar{Y}_{12..} - \bar{Y}_{21..} = \alpha_{11}^{AB} + \alpha_{22}^{AB} - \alpha_{12}^{AB} - \alpha_{21}^{AB}$$

which involves only the AB interaction (and of course the neglected $\varepsilon$ terms).

2. Interactions which involve color but not chlorine still give valid tests, but less powerful tests, e.g.,

$$SSBC = 2(\bar{Y}_{\cdot 11\cdot} + \bar{Y}_{\cdot 22\cdot} - \bar{Y}_{\cdot 12\cdot} - \bar{Y}_{\cdot 21\cdot})^2$$

and

$$\bar{Y}_{\cdot 11\cdot} + \bar{Y}_{\cdot 22\cdot} - \bar{Y}_{\cdot 12\cdot} - \bar{Y}_{\cdot 21\cdot} = (\alpha_{11}^{BC} + \alpha_{22}^{BC} - \alpha_{12}^{BC} - \alpha_{21}^{BC})/2$$

3. The color chlorine interaction simply tests the main effect due to color:

$$SSAC = 2(\bar{Y}_{1\cdot 1\cdot} + \bar{Y}_{2\cdot 2\cdot} - \bar{Y}_{1\cdot 2\cdot} - y_{2\cdot 1\cdot})^2$$

and

$$\bar{Y}_{1\cdot 1\,\cdot} + \bar{Y}_{2\cdot 2\,\cdot} - Y^{-}_{1\cdot 2\cdot} - \bar{Y}_{2\cdot 1\cdot} = \alpha_1^{C} - \alpha_2^{C}$$

# APPENDIX C

## RING OVEN PROCEDURES USED IN STATISTICAL EVALUATION

# APPENDIX C

## RING OVEN PROCEDURES USED IN STATISTICAL EVALUATION

Presented here are the procedures used in the fractional factorial and the qualifications testing for the ions zinc, calcium, magnesium, iron copper, lead, chloride, fluoride, nitrate and sulfate. These procedures were for laboratory use only. Further clarification of the procedures will be required before incorporation into a field test kit instruction manual.

### ZINC PROCEDURE

14 mm attachment

Whatman No. 40 Filter Paper

1. Apply 15 µl sample. Dry.
2. Apply 5 µl 3M hydrochloric acid.
3. Apply 2 µl 1M thioacetamide.
4. Wash to ring with 5 to 10 µl 3M hydrochloric acid.
5. Fume over concentrated ammonium hydroxide for 30 seconds.
6. Place 22 mm attachment on ring oven. Replace filter.
7. Apply 15 µl 1.5M ammonium hydroxide.
8. Wash to 22 mm ring with 20 to 30 µl deionized water. Dry.
9. Spray with PAN reagent (0.3g pyridylazonaphthol in 100 ml of 0.25% formic acid in methanol). Dry. Bathe quickly in 15% ammonium acetate. A red-purple ring at the 22 mm ring zone indicates zinc.

## CALCIUM PROCEDURE

14 mm attachment

What No. 40 Filter Paper

1. Apply 50 µl sample, keeping within as small an area as possible. Dry.
2. Bathe filter for five minutes in a solution containing 1 g ammonium carbonate per 10 ml 1:1 ammonium hydroxide-water.
3. Remove from bath, rinse in deionized water. Dry.
4. Place filter on ring oven. Wash out to ring zone with 30 µl 0.1M HCl. Dry.
5. Bathe rapidly in reagent solution, containing saturated bis-glyoxyl(hydroxyanil) in ethanol, 10% carbonate, and 10% sodium hydroxide in the ratio of 4:1:1. A dark red ring at the 14 mm ring indicates calcium.

## MAGNESIUM PROCEDURE

22 mm attachment

Whatman No. 40 Filter Paper

1. Apply 15 µl sample.
2. Wash to ring zone with 20 to 30 µl 0.1M hydrochloric acid. Dry.
3. Bathe for 5 minutes in Magneson solution (0.001 g p-nitrophenylazo - resorcinol in 100 ml 2M sodium hydroxide). A blur ring at the 22 mm ring zone indicates magnesium.

## IRON PROCEDURE

14 mm attachment

Whatman No. 541 Filter Paper

1. Apply 15 µl sample.
2. Wash to ring zone with 15 µl nitric acid prepared by fuming deionized water with Ultrex nitric acid in a desiccator. Dry.
3. Swab on Ferrozine reagent. A purple ring at the 14 mm ring zone indicates iron.

## COPPER PROCEDURE

14 mm attachment

Whatman No. 40 Filter Paper

1. Apply 50 µl sample in as small an area as possible.
2. Wash to 14 mm ring with 50 µl 3M ammonium hydroxide containing 1 g ammonium carbonate per 100 ml. Dry.
3. Spray on dithiooxamide solution (1% in acetone) and blow ring gently until dry. An olive green ring at 14 mm ring zone indicates copper.

# LEAD PROCEDURE

14 mm attachment

Whatman No. 40 Filter Paper

1. To a 10 ml sample, add 10 mg potassium cyanide. Mix well.
2. Run a portion of this solution into a glass wool-plugged eyedropper containing one inch of a strongly basic anion exchange resin, $OH^-$ form. Let sit on column for 5 minutes.
3. Collect column effluent in a clean container.
4. Apply 50 µl sample to ring oven.
5. Wash to ring zone with 30 µl nitric acid fumed water (pH $\cong$ 1). Dry.
6. Fume over concentrated hydrochloric acid for 3 minutes.
7. Swab on saturated solution of thiazolylazonaphthol in isopropyl ether. Dry.
8. Fume over concentrated ammonium hydroxide for 1 minute.
9. Wait 5 minutes, then compare with standard rings. A purple ring at 15 mm indicates lead.

## CHLORIDE PROCEDURE

33 mm attachment

Whatman No. 541 Filter Paper

1. Apply rapidly 100 μl deionized water. Dry.
2. Place 22 mm attachment on ring oven. Replace filter.
3. Apply 15 μl sample. Dry.
4. Wash to ring zone with 20 to 30 μl deionized water. Dry.
5. Apply 15 μl 0.35M silver nitrate. Dry.
6. Wash to ring zone with 20 to 30 μl deionized water. Dry.
7. Using 33 mm attachment, recenter filter.
8. Apply 50 μl 3M nitric acid.
9. Apply 50 μl deionized water. Dry.
10. Spray with 0.35M silver nitrate. Expose to ultraviolet light for 10 minutes. A brown ring at the 22 mm ring zone indicates chloride.

## FLOURIDE PROCEDURE

14 mm attachment

Whatman No. 40 Filter Paper

1. Place 0.005 g thorium chloranilate, 50 μl methyl cellosolve, and 400 μl sample in plastic vial. Cap and shake vigorously. Allow to equilibrate for one-half hour.
2. Apply 50 μl sample from vial to ring oven.
3. Wash to the ring zone with 50 μl deionized water. Dry.
4. A purple-brown ring at the 14 mm ring zone indicates fluoride.

## NITRATE PROCEDURE

14 mm attachment

Whatman No. 40 Filter Paper

1. Apply 15 μl sample. Dry.
2. Apply 15 μl deionized water. Dry.
3. Apply 30 μl 0.1M barium chloride. Dry.
4. Apply 15 μl deionized water.
5. Place 22 mm attachment on ring oven. Replace filter.
6. Apply 15 μl 1% Ultrex hydrochloric acid.
7. Wash to ring zone with 20 to 30 μl deionized water. Dry.
8. Using a glass wool swab, gently swab ring with diphenylbenzidine reagent (0.01 g in 50 ml concentrated sulfuric acid). A dark blue ring at the 22 mm ring zone indicates nitrate.

## SULFATE PROCEDURE

14 mm attachment

Whatman No. 40 Filter Paper

1. Apply 5 μl sample.
2. Wash to ring zone with 15 μl deionized water.
3. Apply 30 μl 0.1M barium chloride. Dry.
4. Wash to ring zone with 15 μl deionized water. Dry.
5. Place 22 mm attachment on ring oven. Replace filter.
6. Apply 15 μl 1% Ultrex hydrochloric acid, followed by 15 to 20 μl deionized water, washing to ring. Dry.
7. Bathe for one minute in deionized water.
8. Bathe for ten minutes in a freshly prepared saturated potassium rhodizonate solution. A red-brown ring at the 14 mm ring zone indicates sulfate.

# APPENDIX D

# TYPICAL EQUIPMENT FOR A PROTOTYPE RING OVEN FIELD TEST KIT

# APPENDIX D

## TYPICAL EQUIPMENT FOR A PROTOTYPE RING OVEN FIELD TEST KIT

| Quantity | Item |
|---|---|
| 1 each | Trace Oven, Thomas 9430-E10 |
| 1 each | Trace Oven Adapter, 22 mm i.d., Thomas 9430-E53 |
| 1 each | Trace Oven Adapter, 14 mm i.d., Thomas 9430-E62 |
| 1 each | Plastic Coating Kit, PTFE, Thomas 7805-D20 |
| 1 each | Twenty microliter digital pipette, Rainin P-20 Pipetman |
| 1 box | *Disposable Microliter Pipette Tips, Rainin C-20, 1000/box* |
| 5 each | Petri dishes |
| 5 boxes | Whatman #40 Filter Paper, 5.5 cm |
| 5 boxes | Whatman 540 Filter Paper, 5.5 cm |
| 1 each | Ultraviolet Flashlight with batteries |
| 1 set | Permanent Standard Rings |
| 5 each | 100 ml beakers |
| 1 liter | Deionized Water, High Purity |
| 100 ml | Three molar hydrochloric acid |
| 100 ml | One molar thioacetamide |
| 100 ml | Concentrated ammonium hydroxide |
| 100 ml | 1.5 molar ammonium hydroxide |
| 200 ml | PAN in methanol-formic acid, aerosol spary |
| 100 ml | 0.1 molar hydrochloric acid |
| 200 ml | Magneson |
| 100 ml | 3M ammonium hydroxide, ammonium *carbonate added* |
| 200 ml | Dithiooxamide aerosol, 1% in acetone |
| 100 ml | *50% ammonium hydroxide + 10 g ammonium carbonate* |
| 100 ml | 10% sodium hydroxide |
| 100 ml | 10% sodium carbonate |
| 200 ml | Glyoxal bis(hydroxyanil), saturated in ethanol |
| 100 ml | 0.1M barium chloride |
| 100 ml | 15% Ultrex hydrochloric acid |
| 5 g | Potassium Rhodizonate |
| 100 ml | 0.35 M silver nitrate |
| 100 ml | 3M nitric acid |
| 200 ml | 0.35M silver nitrate, aerosol spray |
| 1 each | Instruction Manual |

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