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A SYSTEM TO ANALYZE WATER FOR POTABILITY

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FOREWORD

This study was initiated by the Biomedical Laboratory of the Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio. The research was conducted by Ionics Incorporated, 65 Grove Street, Watertown, Massachusetts 02172, under Contract AF33(615)-2877. The work was performed in support of Project 6373, "Equipment for Life Support in Aerospace," and Task 637304, "Waste Recovery and Utilization." Mr. A.B. Hearld of the Biotechnology Branch, Life Support Division was the contract monitor for the Aerospace Medical Research Laboratories.

The principal investigator for Ionics was Dr. John L. Eisenmann, Manager of Membrane Technology in Ionics Research Division, assisted by Mr. Alan S. Graff, Project Chemist and Mr. Robert M. Potter, Chief Division Engineer of Ionics Electronics Division. The work described in this report was carried out under the supervision of Mr. W.A. McRae of Ionics, Vice President for Research, and was performed between April 1965 and February 1967.

This technical report has been reviewed and is approved.

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ABSTRACT

Methods were developed by which an astronaut will be able, during an aerospace mission, to analyze water reclaimed from urine, fuel cells and dehumidification water, to determine if the water conforms to certain standards. This was accomplished by the use of specific-ion electrodes and special conductivity cells using standard pH and reference electrodes. Unique manifolding and circuitry were designed and integrated with the sensors. All system components were housed in a lightweight, portable instrument case with easy accessibility.

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SECTION I

INTRODUCTION

The purpose of this program was to develop methods by which an astronaut will be able, during an aerospace mission, to analyze water reclaimed from urine, fuel cells, and dehumidification water, to determine if the water conforms to certain standards. These standards were:

Specific Conductivity	Not greater than 500 μ mhos/cm
pH	5.5-8.0
Chlorides (Cl^-)	Less than 450 ppm
Fluorides (F^-)	Less than 2.5 ppm

At the beginning of the effort, a sulfate standard of less than 200 ppm was used in place of the fluoride standard. The reason for changing to the fluoride standard is explained in Section III.

Conformance to the standards was to be indicated by a visible or audible signal such as: the movement of a pointer, a light, a change in color or a buzzer. The analytical methods were to be suitable inter alia for use at 15°C to 28°C, pressures to 380 mm Hg to 620 mm Hg, humidity levels of 30% to 80% relative, a weightless environment, and radiation within established limits for human occupancy.

The laboratory model was to be of nontoxic, nonirritating, corrosion-resistance materials. Consideration was to be given designs that would withstand impacts of 25 "G" axial and 10 "G" lateral. Power for the model was limited to 100 watts. The weight was not to exceed 50 pounds.

Ionics proposed to develop the required potability detector for the four functions of interest by transistorizing and miniaturizing current instrumental methods for pH and conductivity measurements, while adapting, by use of appropriate instrument modification and redesign, absorption bands in the ultraviolet, infrared and visible spectral regions for use in the quantitative determination of sulfate and chloride ions. However, as described in Section II, analysis via light absorption by ionic species was determined to be too complex for this application. The recently available sulfate and chloride ion-specific electrodes promised a more rapid, simple, accurate, and sensitive analytical technique. Consequently, an all-electronic water potability meter employing specific-ion electrodes for chloride and sulfate (ultimately fluoride) analyses was designed.

A water potability meter was built within the specifications delineated above. Indication of acceptability of the water was via a red-green go-no go light. This meter was tested with synthetic water and field water samples* provided by Ionics' Analytical Section. Delivery of the meter to the Aerospace Medical Research Laboratories was accomplished in February 1967. An operating and maintenance manual was supplied with the model.

* Samples from numerous Ionics water demineralizing plants in the United States, North Africa, and the Middle East.

SECTION II

SPECTROSCOPY

The use of infrared absorption as a feasible method for analysis of the sulfate ion was first demonstrated by use of a modified potassium bromide disk technique [Han Tai and A. L. Underwood Anal. Chem. 29, 1430 (1957)]. In this method, sufficient KBr to give the final disk the desired weight is added to an aliquot of an aqueous sulfate solution. The mixture is then freeze-dried overnight, the powder pressed into a disk and its spectrum recorded in the usual manner. The sulfate band was observed at 9μ and shown [L. Citron, Han Tai, R. A. Day, Jr. and A. L. Underwood, Talanta 8, 798(1961)] to be useful in the determination of sulfate in the presence of nitrate and nitrite ions.

Subsequent investigations [A. L. Underwood, M. W. Miller and L. H. Howe, III, Anal. Chem. Acta. 29, 79(1963)] have extended the study of sulfate infrared spectrophotometry to the use of aqueous solutions themselves. This is made possible by constructing absorption cells with windows of BaF₂, AgCl, or the relatively new commercial material, Irtran II.

With such aqueous solutions, the sensitivity in terms of concentration appears to be much lower, and there is a broadening of the absorption bands as compared with potassium bromide disks. Therefore, the original communication on this subject described measurements on solutions containing milligram quantities per milliliter; whereas the KBr disk technique involved microgram amounts. However, Beer's law is followed over the absorption range investigated with an average relative deviation from known concentrations of 3%. The sulfate-band position was cation-independent: potassium, sodium, lithium, zinc, and cadmium sulfates yielded identical spectra, and the absorbance values depended only on the sulfate concentration. Some inorganic anions may interfere in this region of the spectrum. The technique was suggested as being useful in certain special applications.

The foregoing indicates that use of sulfate ion absorption to determine water potability would require operation in the 9-micron region, would need no modification of the aqueous sample solution, but would necessitate the use of special absorption cells.

In aqueous solutions the chloride ion absorbs in the ultraviolet at approximately 180 millimicrons. Measurement of chloride absorption must, therefore, be done using advanced optical and electronic components designed for the far-ultraviolet. These include a special hydrogen discharge lamp as a source and a modified photomultiplier tube as detector. Instrument optics and absorption cells must be constructed from far-ultraviolet silica and coated with magnesium fluoride. Purging with nitrogen or helium is also required in order to remove oxygen and water vapor from the optical path. Some of these instrumental difficulties can be overcome by a bathochromic shift of the maximum absorption band for the chloride ion, and it has been demonstrated [J. Jortner and A. Treinin, Trans. Faraday Soc. 58, 1503(1962)] that the chloride band is shifted

Conclusions

to ~ 195m μ when measured in acetonitrile. This wavelength is within the range of standard ultraviolet instrumentation. Use of chloride ultraviolet absorption in a water potability detector would, therefore, seem to require either use of special far-ultraviolet equipment or employment of a special solvent to shift the wave length to a more accessible region. The latter alternative would require excessive manipulation for the present application.

SECTION III

SPECIFIC-ION ELECTRODES

In view of the complications and uncertainties that seem to exist in the application of absorption spectroscopy to the detection of sulfates and chlorides in water, a search was made simultaneously for alternative ways to accomplish these analyses. We especially wanted to uncover more direct and simple techniques, if any existed, before embarking on the spectrometric approach. It appeared that such a simple technique could be developed via the use of specific-ion electrodes for both chloride and sulfate. The specific-ion electrode technique would employ a silver billet electrode coated with silver chloride to determine chloride and would employ the newly available sulfate-specific electrode for sulfate determination. The latter electrode has a silicone rubber precipitate membrane to contact the solution to be measured.

Chloride Electrode

This is a metallic electrode with a large area of silver metal to provide rapid electrode response, increased thermal stability, and minimum polarization effects. For the determination of the chloride ion concentration of a sample solution the silver is coated electrolytically with silver chloride. With the silver chloride coating on the silver electrode, the Ag^+ and Cl^- concentrations are related by the solubility product of silver chloride, and the potential developed by the electrode is:

$$E = E^{\circ} - 0.0591 \log(\text{Cl}^-), \text{ at } 25^{\circ}\text{C}$$

A typical chloride calibration curve is shown in Figure 1. The voltage of the silver-silver chloride electrode relative to a saturated calomel reference electrode is plotted against known ppm of chloride. Good correlation is observed between the recorded millivolt reading and the chloride concentration over the range of interest: less than 450 ppm chloride ion. In regard to the requirements for potability as defined for this program, solutions containing chlorides at the 450 ppm level will normally have conductivities substantially greater than the 500 μmhos limit and thus be rejected on this basis as well as by the chloride concentration limit of 450 ppm.

Table I compares the results of field water samples analyzed by the use of the silver-silver chloride electrode and the results from the standard Mohr volumetric method. In all these very different waters, the specific chloride electrode gave chloride values that differed by less than 20 ppm from those obtained by standard analyses.

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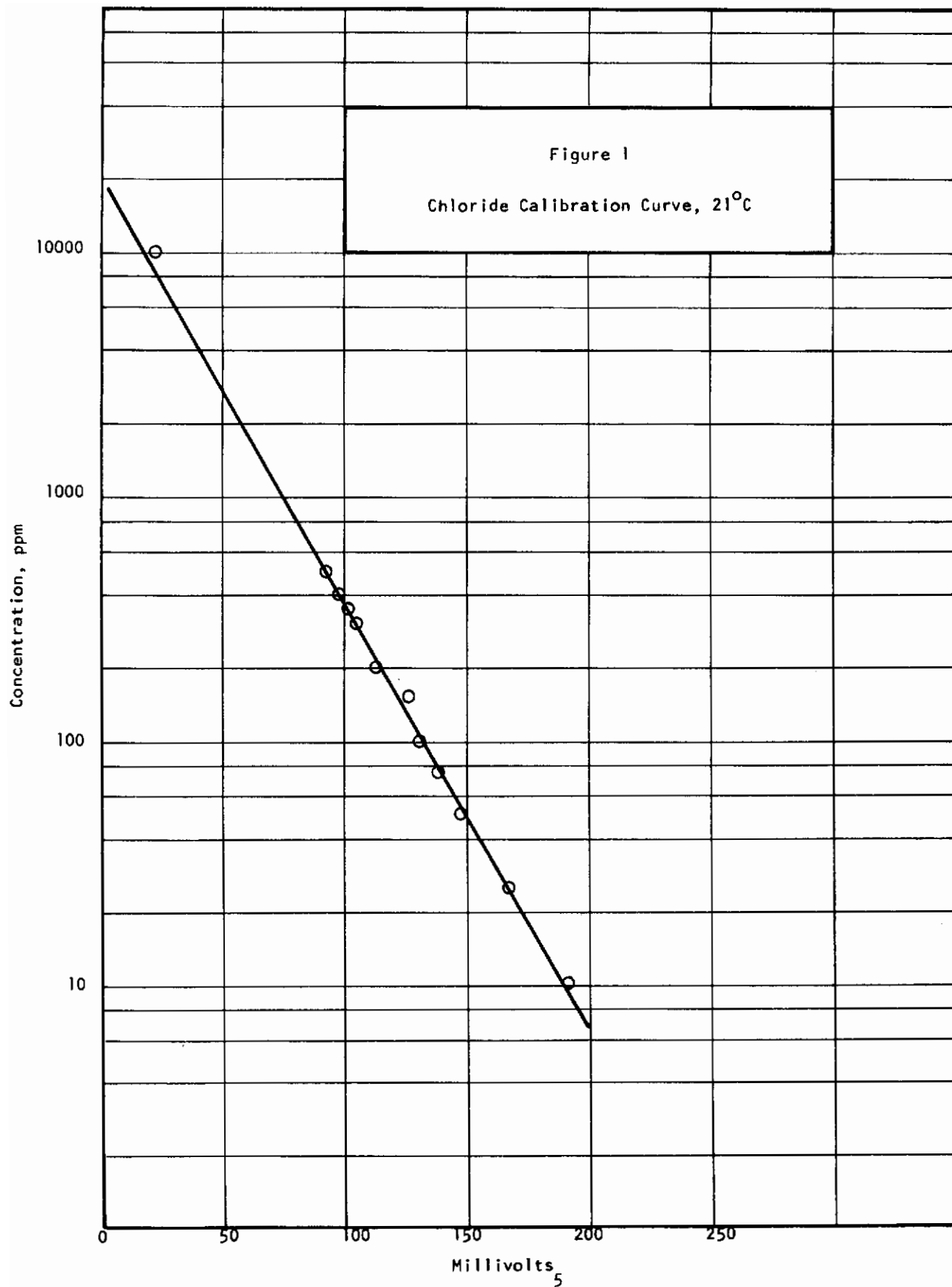


Table I

Sample No.	Standard Analyses					Chloride by Specific Electrode ppm	Absolute Difference Between Chloride Analyses, ppm
	Cation (ppm)		Anions (ppm)				
	Calcium	Sodium	Sulfate	T.D.S.	Chloride		
1	58	373	467	1400	290	310	20
2	6	27	16	148	28	39	11
3	29	125	127	528	149	162	13
4	115	182	138	1095	325	325	0
5	613	110	130	3014	85	92	7
6	98	283	513	1285	269	280	11
7	157	129	167	1165	312	300	12
8	12	88	95	352	49	54	5
9	115	182	138	1095	323	332	10
10	28	600	37	1862	88	82	6

Sulfate Electrode

The sulfate electrode was supplied by National Instrument Laboratories, Inc.* It has a silicone rubber, heterogeneous membrane packed with a precipitate of barium sulfate. The size, form and method of precipitation and amount of precipitate are all critical for the proper functioning of the electrode [Pungor, Havas and Toth, Acta Chim. Acad. Sci. Hung. 4], 239(1964)]. Similarly to the chloride electrode, its potential depends on the activity of the specific ion according to the Nernst equation and is related to the physical-chemical characteristics of the electrode.

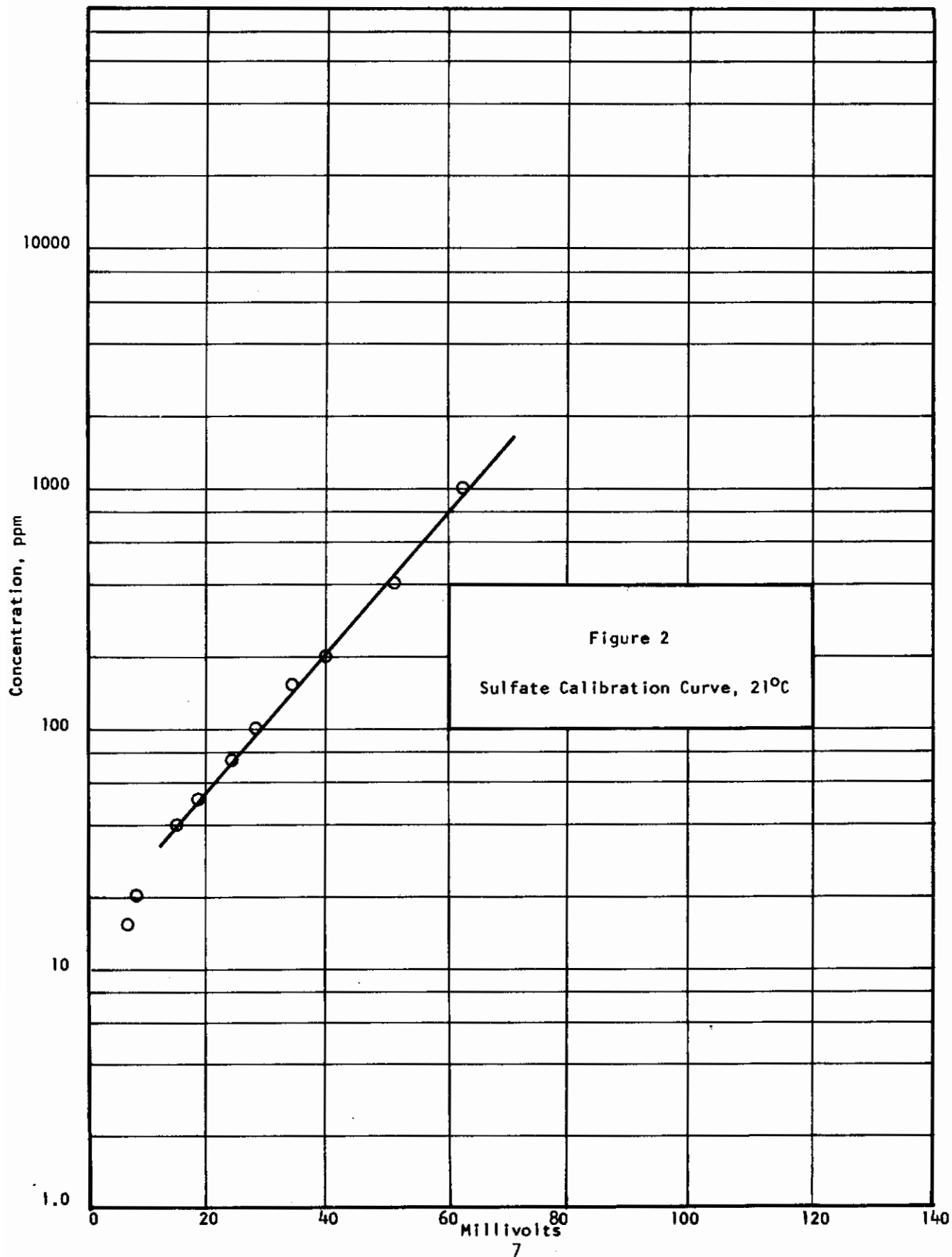
Figure 2 shows that a sulfate-specific electrode also gives an excellent correlation between sulfate concentration and millivolt reading. However, the sulfate electrode used to determine the curve in Figure 2 was from an experimental production batch and was not suitable for the direct determination of sulfate in the presence of foreign salt of a concentration higher than 10^{-3} mols/liter. At higher concentrations the electrode responds to the total anion concentration rather than specifically to sulfate.

Because of the difficulty in the timely procurement of a satisfactory sulfate-specific electrode and the decline in importance of sulfate-ion analyses relative to other anions, a decision was made to replace the sulfate specification with one for fluoride, an ion which can also be determined via a specific electrode.

Fluoride is naturally present in some drinking waters and, in low concentrations beneficial in preventing dental caries. Supplementation of fluoride in drinking water is practiced in areas where little or no fluorides are present. Optimum concentration is on the order of 1 ppm and concentrations greater than twice the optimum value constitute grounds for rejection of the water supply. One source of fluoride in

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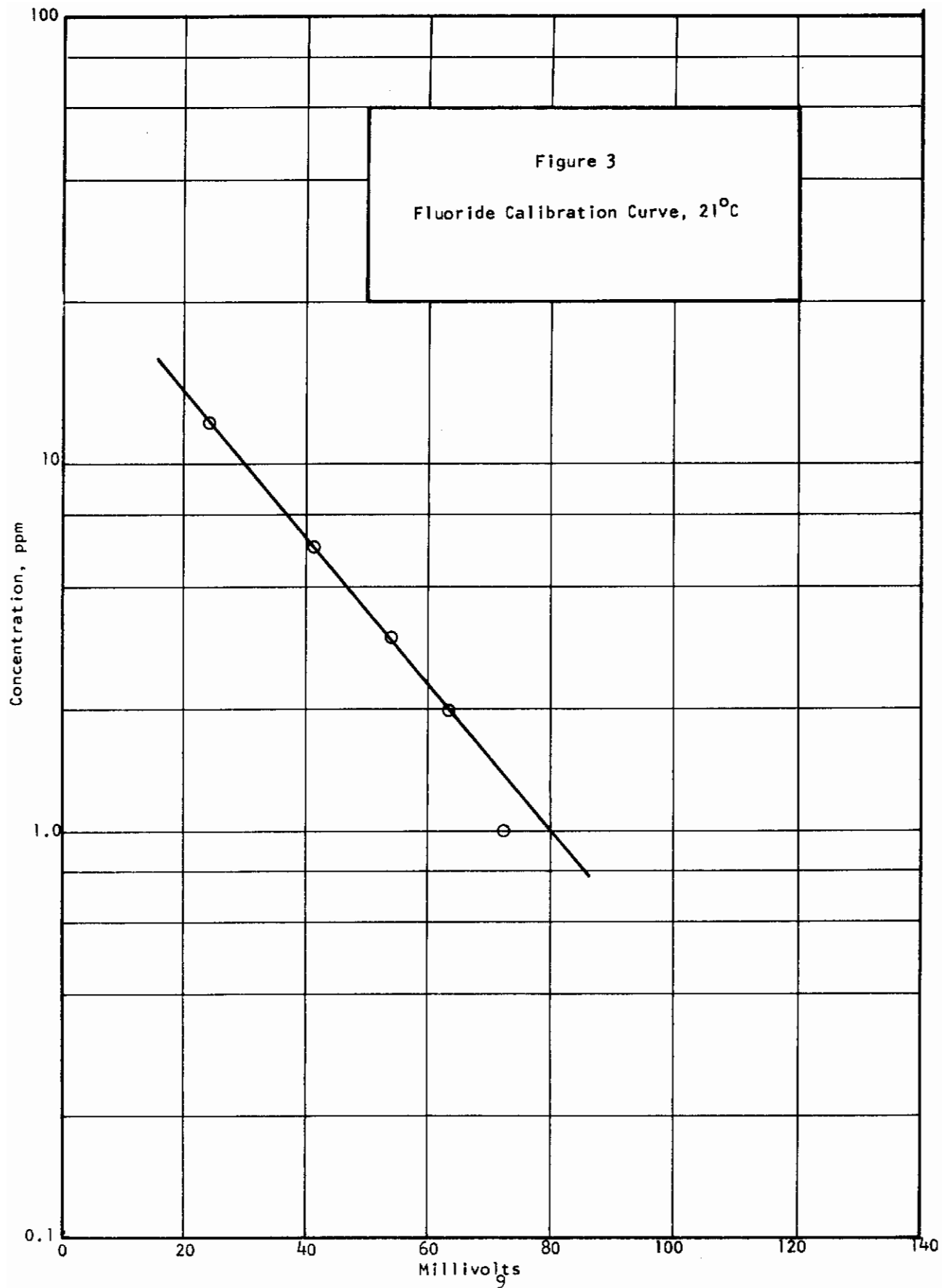
a space vehicle would be a leak in a refrigeration loop. Freon would be released to the atmosphere and eventually consumed in the toxin burner with formation of hydrogen fluoride. When the products of the toxin burner are condensed to recover water vapor, fluoride would be dissolved in the condensate. In this case the potability meter would indicate not only the presence of contamination but also its source.

Fluoride Electrode

The fluoride electrode is a solid-state membrane electrode in which the conducting membrane is a laser-type, rare-earth doped single crystal. It exhibits high specificity for fluoride ion even in the presence of over a ten-thousand fold excess of most other common anions. It is housed in a high-strength, plastic body and is virtually immune to attacks by acids and bases. Hydroxide ion causes the only known significant interference; then, only if the hydroxide ion activity exceeds the activity of the fluoride ion.

Figure 3 shows an example of typical calibration data where the fluoride concentration is plotted against millivolts.

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pH AND CONDUCTIVITY PROBES

pH Electrode

The pH electrode is a standard glass electrode. It consists of an internal sealed tube with a metallic tip and an external tube containing a standard solution which contacts the metallic tip. The reference electrode used with the glass electrode - and with the specific-ion electrodes - is a saturated calomel electrode using a fiber junction for electrical contact with the test solution.

Figure 4 shows the correlation between pH and millivolt readings for a series of standard buffer solutions at 21°C. Table II compares the results reported on field water samples, using laboratory instrumentation, with those obtained from the same samples by the meter electrodes and the calibration curve (Fig.4).

TABLE II

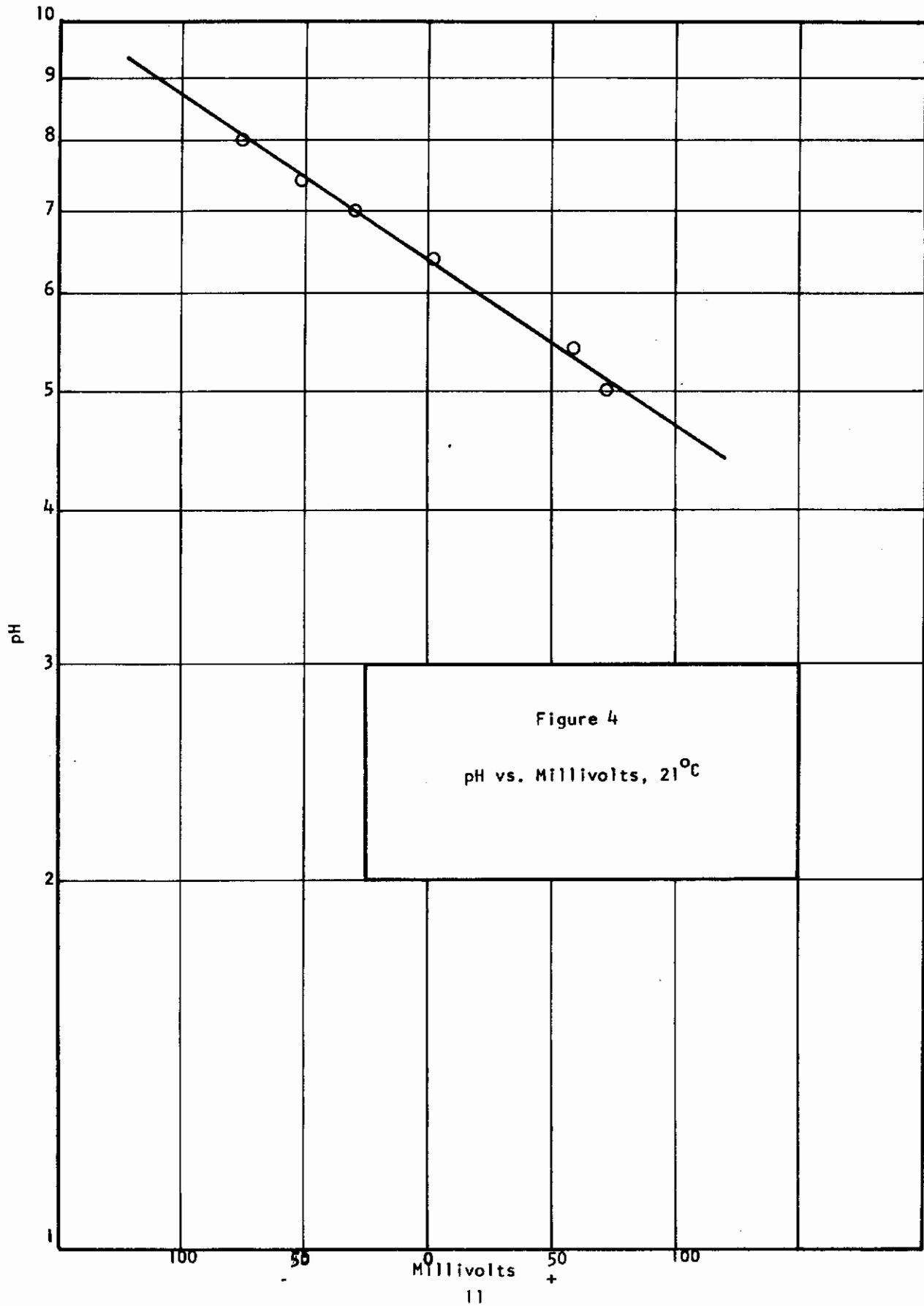
Sample #	Reported pH	Reading MV	pH from Curve
1	8.4	-95	8.6
2	7.3	-75	8.0
3	7.5	-65	7.8
4	8.1	-76	8.1
5	7.2	-43	7.3
6	8.5	-118	9.2
7	8.2	-78	8.2
8	8.7	-71	7.9
9	8.3	-91	8.4
10	8.4	-97	8.6

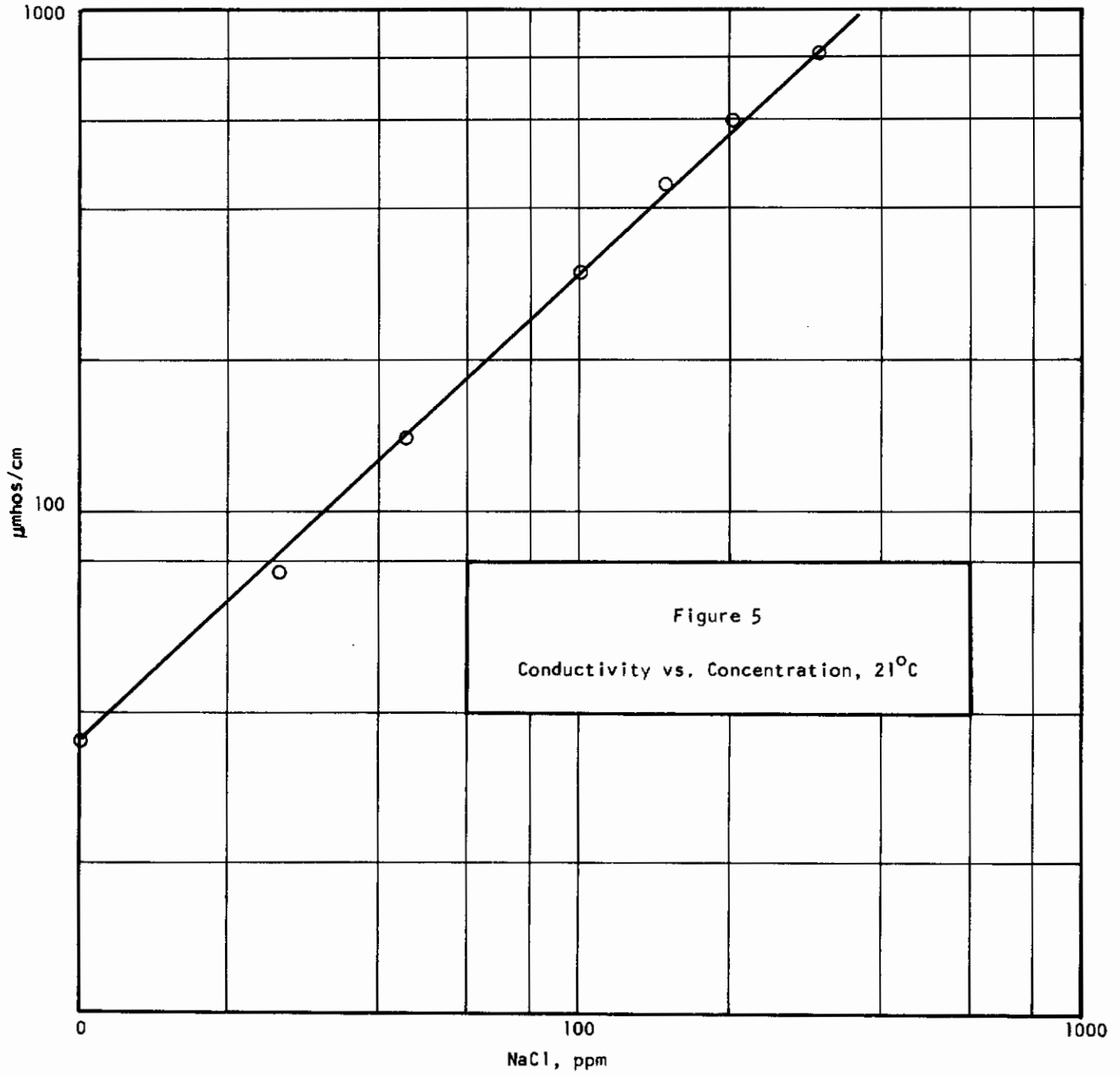
Conductivity Cell

The miniature conductivity cell is a specially designed unit constructed by Industrial Instruments Inc.* and recommended by them for applications where space is a limiting factor. It is fabricated from epoxy resin, has platinum electrodes, and is 4.5 cm overall length with a diameter of 0.64 cm. The cell constant is 0.2 cm⁻¹ and it can be used to a temperature of up to 100°C. A typical salt concentration - conductivity curve is given in Figure 5.

* Cedar Grove, N.J.
(Beckman Instruments, Inc.)

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DESIGN

General

The laboratory model of the Potability Meter is an all-electronic analytical system based on the response of specific-ion electrodes. All system components are contained in a lightweight, portable, metal instrument case* with overall dimensions of 26 by 21 by 21 cm. The interior is accessible via a hinged, latched top. Weight of the model is approximately 10 pounds (4.5 kg).

A lucite manifold which holds the electrodes is attached directly behind the front panel. Electronic components are mounted on the base and inside rear panel. Red and green lights for go or no-go readout, a rotary switch for measurement selection, and valves and tubing connections for the manifold are mounted on the exterior front panel of the instrument. All meter components were selected for maximum ruggedness compatible with simplicity and ease of adjustment. Figure 6 is a line drawing of the meter, and Figure 7 is a photograph of the completed laboratory model. The meter indicates via a go-no go light signal when a water sample meets or fails to meet the standards: less than 450 ppm chlorides, less than 2.5 ppm fluorides, pH between 5.5 and 8.0, and specific conductivity not greater than 500 μ mhos/cm.

Manifold

The manifold is fabricated from a solid lucite block and is approximately 15 by 5 by 5 cm. The transparency of this plastic permits rapid inspection for electrode damage, fouling, air pockets, channel blockage, etc. The manifold is so designed that the electrodes are at a 45° angle from the vertical, with water, supplied by an external pump, flowing through the length of block at a slight inclination. Both of these arrangements aid in avoiding the formation of air bubbles at the electrode tips. Influent and effluent connections and controlling valves for the manifold are mounted in the block with standard polyethylene tube fittings, using neoprene O-rings to prevent leakage.

This arrangement allows easy and rapid replacement in the event of failure and also the possibility of substitution by other sensing electrodes (e.g., the recently available calcium-specific electrode). Figure 8 is a schematic drawing of the manifold. The manifold with electrodes in place is shown in Figure 9.

Electronics

All active components are solid state, except for read-out lights. Possible conversion to military and/or National Aeronautics and Space Administration specifications served as guide in selecting components. The pH, fluoride and chloride sensing electrodes are self-generating and are connected directly to an amplifier, through a selector switch. The conductivity cell represents a portion of a voltage divider which utilizes a-c power to generate an error signal, a-c power has been selected to minimize the effects of cell polarization. The error signal is coupled to the amplifier through the use of the selector switch mentioned above.

* Bud Cabinet, C-1588. Modified by Ionics

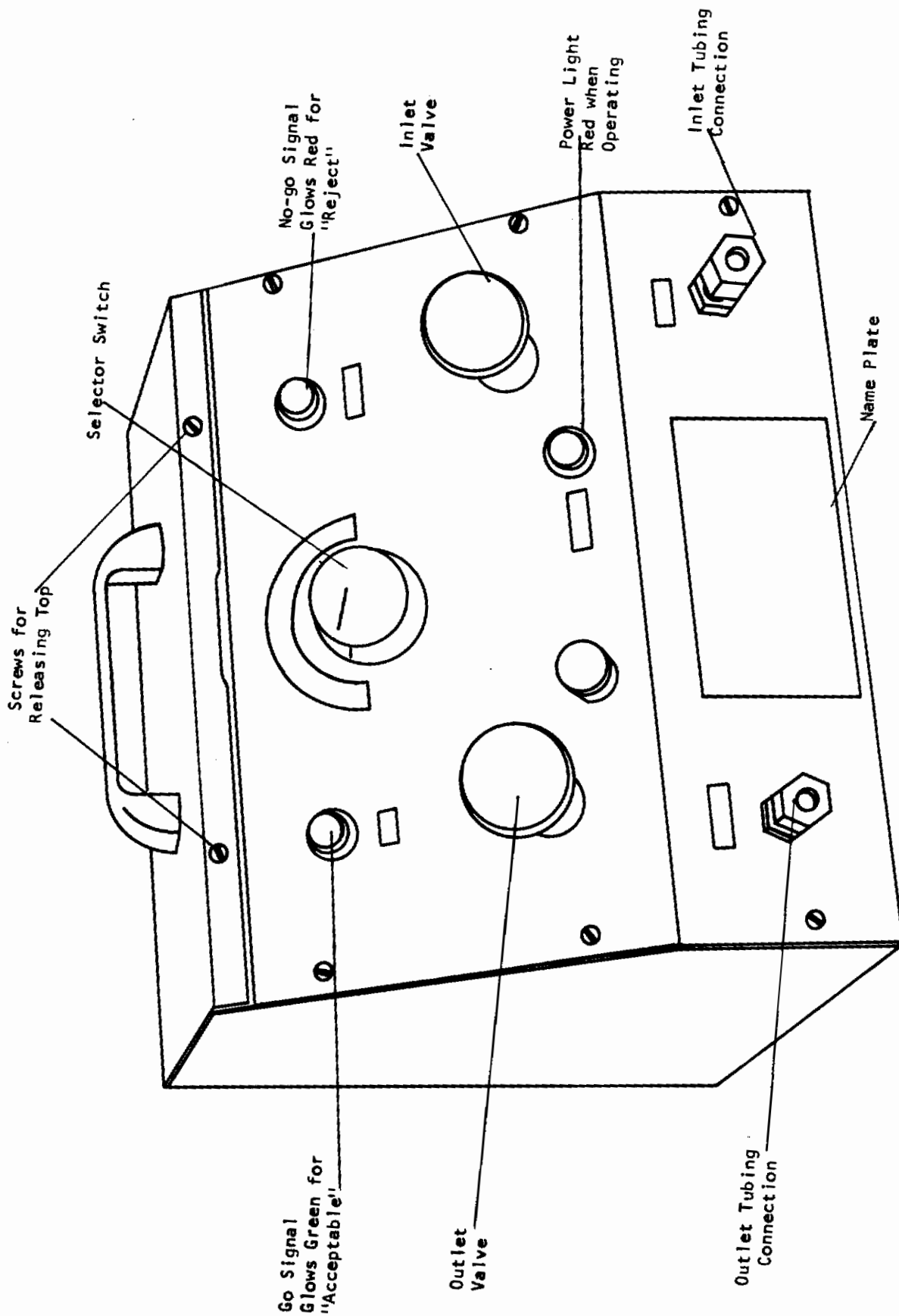


Figure 6
Sketch of Potability Meter

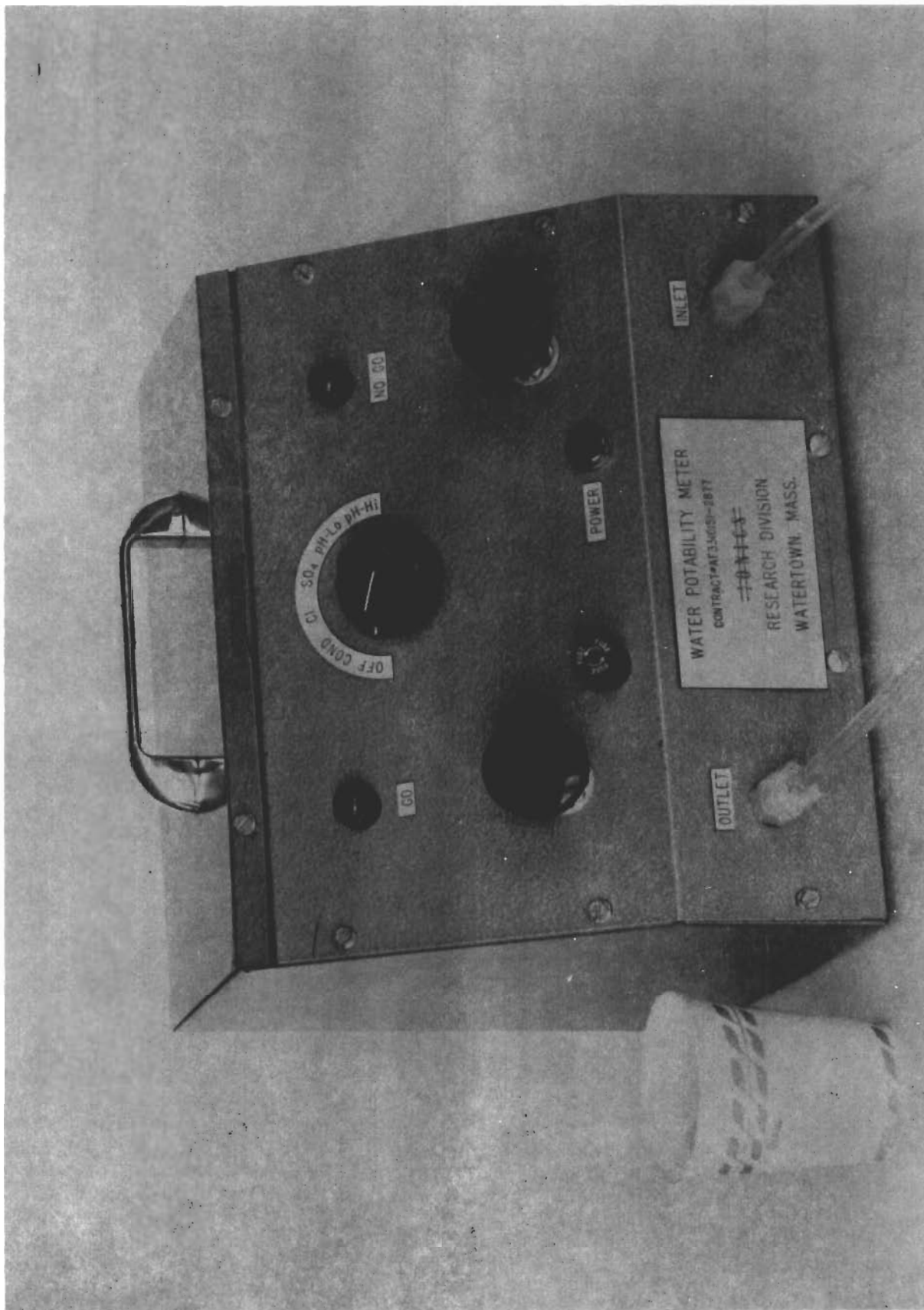


Figure 7
Potability Meter

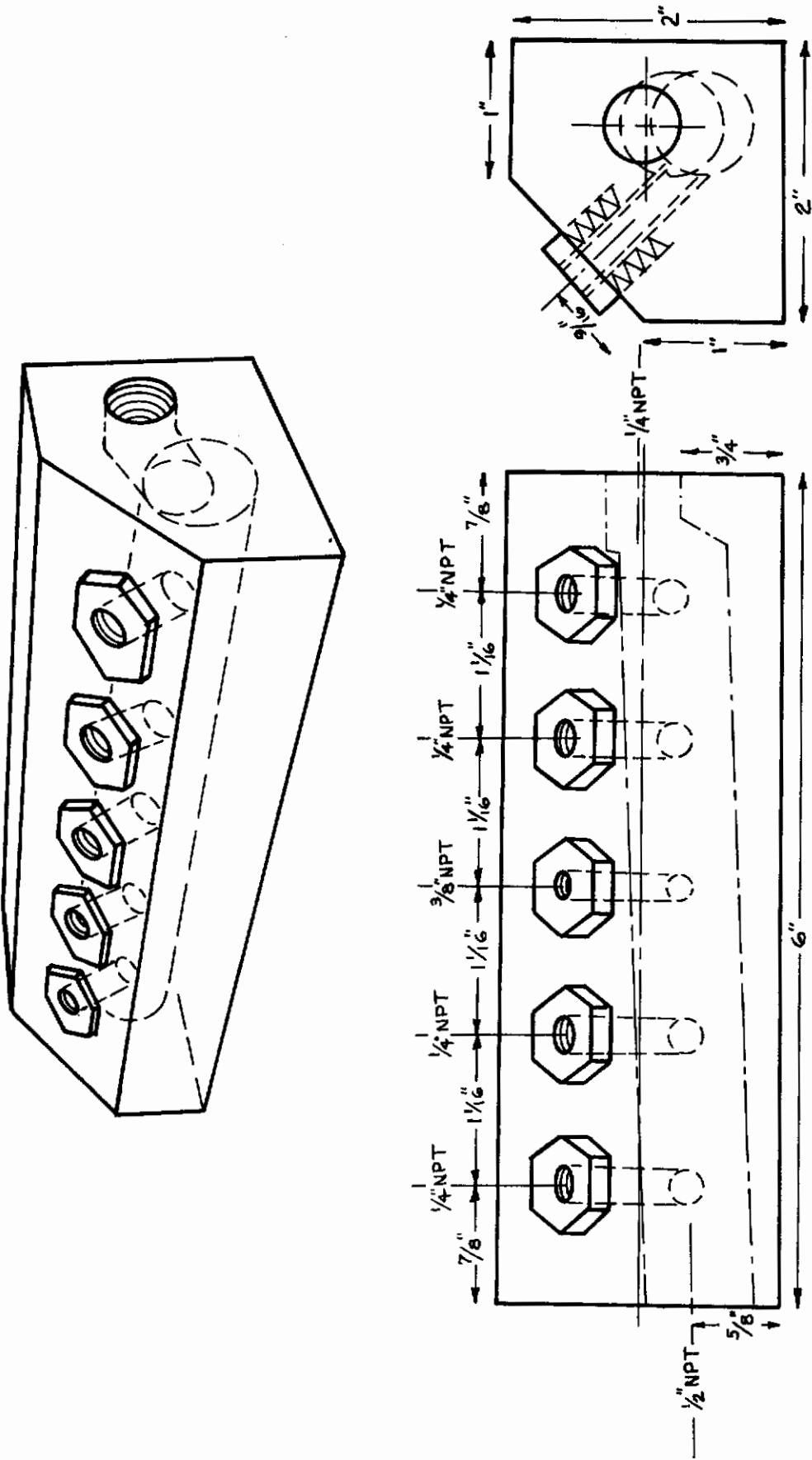


Figure 8
Manifold for Potability Meter

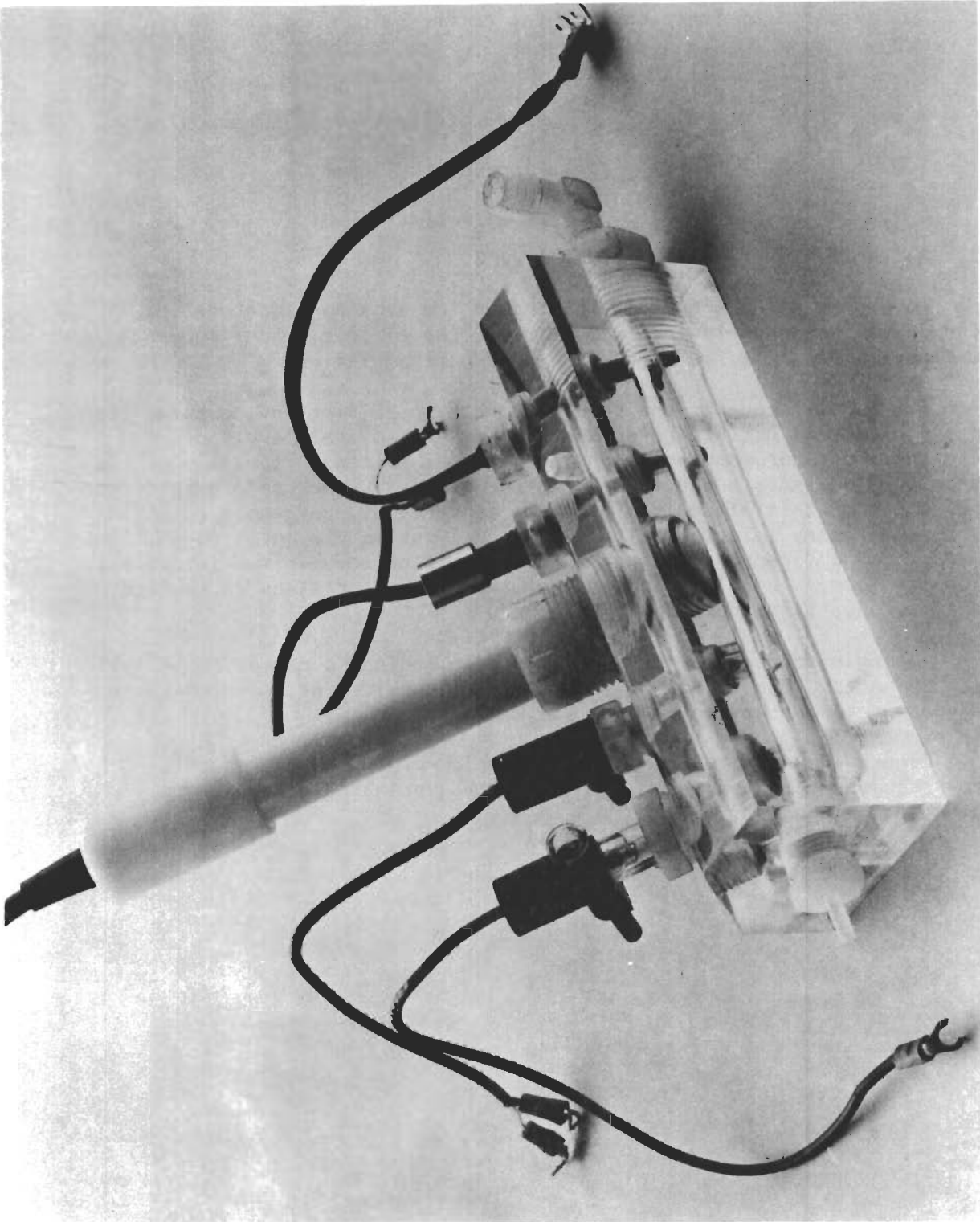


Figure 9
Manifold with Electrodes

A rotary switch is utilized to select each function for measurement and also serve as an on-off power switch. Special care was taken to adequately shield the high impedance lines associated with the sensing electrodes.

The sequence of functions for the rotary switch is:

<u>Position</u>	<u>Function</u>
1	Off
2	Conductivity Limit (500 μ mhos/cm)
3	Chloride Limit (450 ppm)
4	Fluoride (2.5 ppm)
5	pH Low Limit (5.5)
6	pH High Limit (8.0)

All settings are calibrated for 21°C.

To decrease the effect of loading on the sensing electrodes, a high input impedance is incorporated into the circuit. The impedance is developed by using a field effect operational amplifier.

The circuit accepts the signal from the amplifier and compares it to a pre-set, adjustable reference. There are several levels of reference: one for each point on the selector switch. Stability of the reference levels is achieved through the use of a zener reference diode. The output of this stage is digital in content, and reference selection is by the rotary selector switch. The read-out is via go or no-go lights, green for "go", red for "no go". This should ensure minimum interpretation problems. The digital output of the comparator stage is applied to the proper light by a switching circuit.

A single source of input power is utilized and consumption is less than 25 watts. The source is a 60-cycle, 110 volt line. The unit can be adapted to battery operation.

Figure 10, a photograph of the interior of the completed unit, shows the positions of the manifold and the various electronic and switching components.

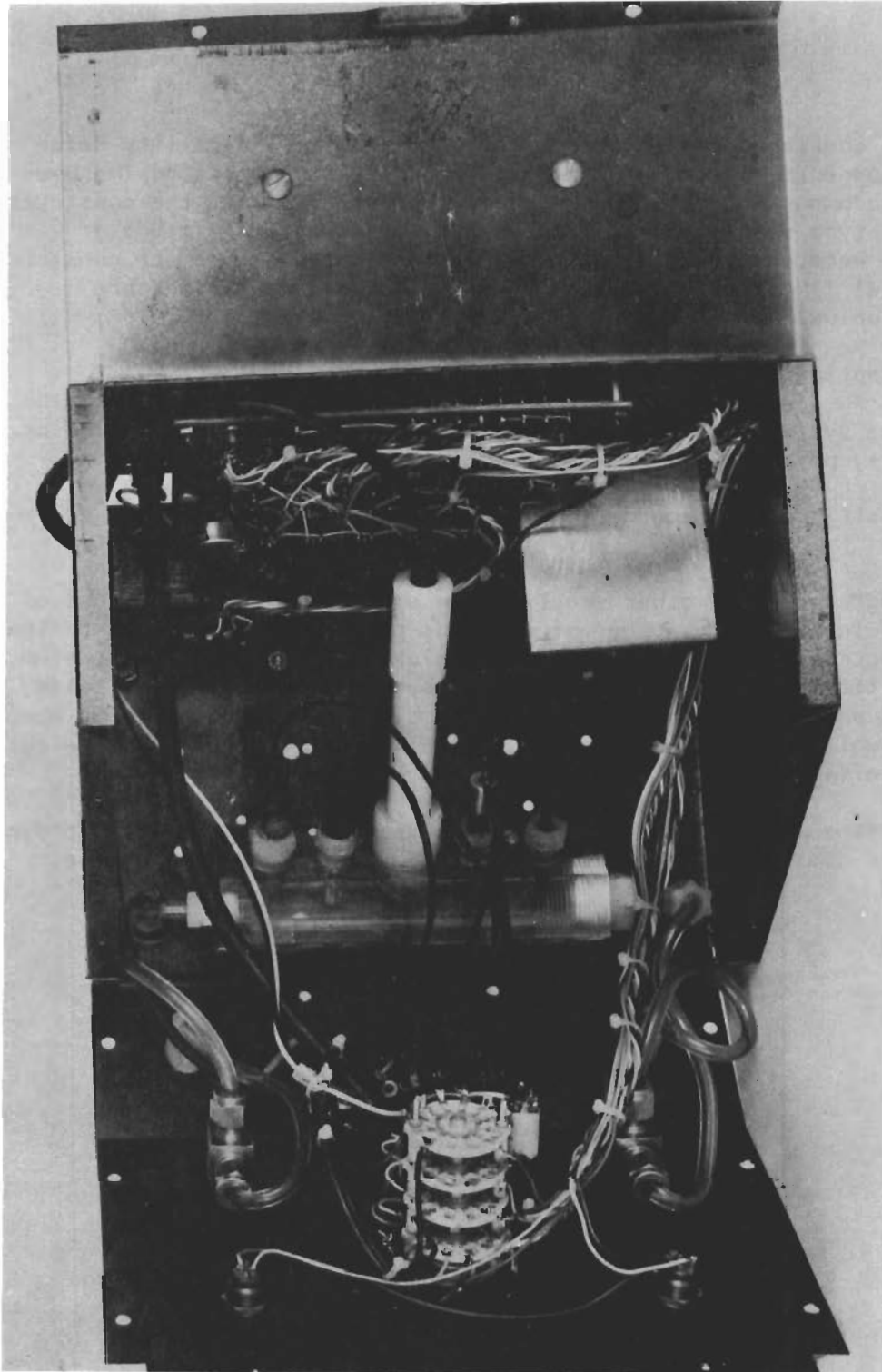


Figure 10
Interior View of Potability Meter

SECTION VI

RECOMMENDATIONS FOR FUTURE STUDY

In the course of designing and testing the Water Potability Meter and its components many modifications of original concepts and improvements in equipment and design were made. However, as with the construction of any prototype system, several areas for possible future study or improvement were uncovered that should be considered before the construction of any "Model II" Water Potability Meter. The recommendations are summarized below:

1. Adaption for use of battery power.
2. The system could have a direct readout in parts per million or moles/liters; pH and millivolt scale could also be provided.
3. A strip chart recorder could be included for continuous monitoring.
4. There are many other specific-ion electrodes available, use of which could increase the number of analyses performed by the meter. These include electrodes specific for bismuth, nickel, copper, antimony, aluminum, potassium, lithium, sodium, calcium, silver, ammonium, sulfide, iodide, bromide and phosphate. To avoid excessive size, a quick-disconnect could be devised which would allow rapid substitution of the appropriate electrode into the manifold.
5. Encapsulation of all electrical components for additional protection against humidity, contamination, radiation and mechanical damage.

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Water Analysis Potability Meter						

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