A CRITICAL STUDY OF
THE PERKIN ELMER FLAME PHOTOMETER (MODEL NO. 18)

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By

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TABLE OF CONTENTS

INTRODUCTION

Although it is difficult to state definitely the date or person who first noticed that emission spectra are characteristic of the various elements present, it has long been common practice in qualitative analysis to make use of the characteristic color produced when the more representative elements are thermally excited. With the development of photoelectric apparatus, considerable effort has been spent in trying to utilize this phenomena in quantitative analysis.

Among the first of these efforts to be successful were those by Jaekel,[1] Lundegardh,[2,3,4,5] Rauterberg and Knippenberg,[6,7,8] Riehm,[9] Schuhknecht,[10]

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[1] Jaekel, I. W., "Lichtelektrisches Messgerat sur Prufung von Kulturboden," *Z. des Vereines Deutscher Ingenieure* 82, pp. 1275-6 (1938).

[2] Lundegardh, H., "Die Quantitative Spektralanalyse der Elemente und ihre Anwendung auf Biologische und Mineralogische Aufgaben," *C. A.* 23:3641.

[3] Lundegardh, H., "Die Quantitative Spektralanalyse der Elemente," *Bull. Brit. Non-Ferrous Metals Research Assoc.* No. 65, p. 24 (1934), *C. A.* 28:3340.

[4] Lundegardh, H., "Quantitative Spectrum Analysis of Metals by Means of Flame and Spark," *Metallwirtschaft* 17, pp. 1222-6 (1938), *C. A.* 33:937.

[5] Lundegardh, H., and Philipson, T., "The Spark-in-Flame Method for Spectral Analysis," *Ann. Agri. Coll.* (Sweden) 5, p. 249 (1938), *C. A.* 32:6576.

[6] Rauterberg, E., and Knippenberg, E., "Potassium Determination by a Photometric Method," *Bodenkunde u. Pflanzenernahr* 20, pp. 364-84 (1940), *C. A.* 36:5108.

[7] Rauterberg, E., and Knippenberg, E., "Determination of Potassium by Photometric Spectroscopy," *Ernahr Pflanze* 37, pp. 73-6 (1941), *C. A.* 36:4052.

[8] Rauterberg, E., and Knippenberg, E., "The Determination of Potassium by Flame Photometric Methods," *Angew. Chem.* 53, pp. 477-9 (1940), *C. A.* 35:706.

[9] Riehm, H., "The Routine Determination of Potash Available to Plants by the Method of Egner and a Special Flame Photometer," *Bodenkunde u. Pflanzenernahr* 28, pp. 246-56 (1942), *C. A.* 37:4180.

[10] Schuhknecht, W., "Spectroanalytic Determination of Potassium," *Angew. Chem.* 50, pp. 299-301 (1937), *C. A.* 31:4921.

Singh and Rao,[11] and Waibel.[12,13] These investigators were chiefly interested in the determination of potassium.

Barnes and his co-workers[14] applied these basic ideas to the determination of both sodium and potassium. The Perkin Elmer Corporation of Glenbrook, Connecticut, commercialized the findings of the latter group by manufacturing and placing on the market their flame photometer, Model No. 18.

Since this flame photometer was presented, the Perkin Elmer Corporation has produced a new model for which they claim more versatility, in addition to some increase in accuracy. The National Technical Laboratories of South Pasadena, California, have placed on the market a more complicated flame photometer to be used in combination with their spectroscope.

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[11] Singh, B. N., and Rao, N. K., "A Photoelectric Photometer for Chemical Analysis," Plant Physio. 13, pp. 419-25 (1938), C. A. 32:7782.

[12] Waibel, F., "Investigation of Materials by Means of Flame Analysis," Z. Tech. Physik. 15, pp. 454-6 (1931), C. A. 29:1735.

[13] Waibel, F., "Optical Arrangement for Spectrographic Analysis of Flames," German Pat. No. 698, p. 664 (Consigned to Siemens and Halske), C. A. 35:6538.

[14] Barnes, R. B., Richardson, D., Berry, J. W., and Hood, R. L., "Flame Photometry, A Rapid Analytical Procedure," Ind. Eng. Chem., Anal. Ed. 17, p. 605 (1945).

OBJECT OF THIS RESEARCH

It is the object of this research to study the operation and accuracy of this instrument. Some of the factors which are assumed to be pertinent to the accuracy and usefulness of the instrument are: Variation of the fuel mixture in the burner, air pressure in the atomizer, flow of solution through the atomizer, fluctuation of line voltage, effect of foreign matter in the air, interference by other elements in the solution, range of concentrations for which the instrument is best suited, fatigue of the photo-cells, amount of solution used, time needed for analysis, reproducibility of instrument readings on the same solution, comparison of analysis by this instrument to analysis by other methods in common use, sensitivity of the galvanometer furnished with the instrument, characteristics of the light filters used, etc.

DESCRIPTION OF THE INSTRUMENT

The flame photometer is designed to analyse for sodium and potassium by use of the thermal emission spectra of these elements. By filtering out colors other than those of certain of the characteristic bright lines of these elements the amount of the element may be determined by measuring with a photo-cell the intensity of the transmitted bright lines.

The instrument is composed essentially of these units: A modified Fisher burner having an especially heavy grid and a fixed air inlet; an atomiser unit which draws the solution from a container, breaks it into a fine mist, and delivers it to the air inlet of the burner; a set of light filters for each element to be determined, passing only that portion of the spectrum containing certain of the bright lines of that element, these being preceded by a water filter to screen out heat and infrared radiation from the photo-cell compartment; a photoelectric cell for each element to be determined; and an electrical unit consisting of a rectifier to produce direct current from the standard alternating current, with suitable condensers, resistances, and a galvanometer arranged in such a way as to enable one to balance the potential from the rectifier against that produced in the photo-cells.

The following, considered with the picture on the next page, will give the reader a better understanding of the controls and external features of the instrument: Upper left is the galvanometer dial. Of the three knobs immediately below it, the left one is used to bring the galvanometer to zero on the standard sodium solution, the center one is the selecter switch, and the right one is used to bring the galvanometer to zero on the standard potassium solution. Immediately below these is the graduated dial. Below

FRONT VIEW OF INSTRUMENT

this is the on-off toggle switch for the electrical circuit. To the left of the toggle switch is the knob used to bring the galvanometer to zero on distilled water when running sodium analyses. To the right of the toggle switch is the knob used for the same purpose when running potassium analyses. At upper center is the air pressure gauge and immediately below it is the air pressure regulator. Below the pressure regulator is a pilot light indicating whether or not the electrical circuit is turned on. Extending above the instrument above the name plate is the vent for burned gases from the burner. Below the name plate is the recess in which to place the container (any standard beaker up to and including 100 ml. may be used) of solution to be fed into the atomizer. On close examination one can see the atomizer intake tube extending down into the beaker.

OPERATION OF THE INSTRUMENT

In operation it is found that the instrument (both burner and electrical circuit) should be turned on and allowed to warm up for approximately an hour before actual readings are taken. The selector switch is set for sodium or potassium as desired at the beginning of the warm-up period. The air pressure is set to the proper value by adjusting the pressure regulator which is built into the instrument. Distilled water is then fed into the atomizer and, with the graduated dial set at zero, the galvanometer reading is brought to zero by adjusting the proper one of the two lower knobs on the panel. Then a standard solution is fed into the atomizer and, with the graduated dial set at 100, the galvanometer reading is brought to zero by adjusting the proper one of the two upper knobs on the panel. The operations described in the last two sentences will at times be referred to in this report as standardizing the instrument. The unknown solution is then fed into the atomizer and the galvanometer reading is again brought to zero, this time by adjusting the graduated dial. The reading on this dial is then translated into parts per million by referring to a graph which has been previously prepared by running various known solutions on the instrument. As used in this report, part per million is defined as a gram per thousand liters of solution.

RANGE OF CONCENTRATIONS PERMISSIBLE

Early in the investigation it was noticed that the graph of instrument readings against parts per million is steepest at low concentrations. Also, the lower the concentration of the high standard solution the more nearly the graph approaches a straight line. These facts are readily seen by a study of Fig's. 1 - 3. The reason for this phenomenon is not fully understood but a possible explanation seems to be that some, at least, of the bright lines of the spectra of sodium and potassium are more or less reversible and at high concentrations appreciable quantities of the light are absorbed by particles in the cooler parts of the flame. In any case, it seems apparent that more accuracy can be obtained on unknowns of fairly low concentrations and using standard solutions of concentrations not greater than 100 parts per million. It is suggested that in operation of the instrument the unknown be first run against a fairly high standard to obtain an approximate analysis. The unknown should then be diluted to a known fraction of the original concentration so that it will give readings between 20 and 80 when run against a standard solution of 50 or 100 parts per million. A more exact analysis will result from these readings. The term, reading or instrument reading, as used in this report refers to the reading indicated on the graduated dial of the instrument when the galvanometer is balanced on zero.

Fig. 1

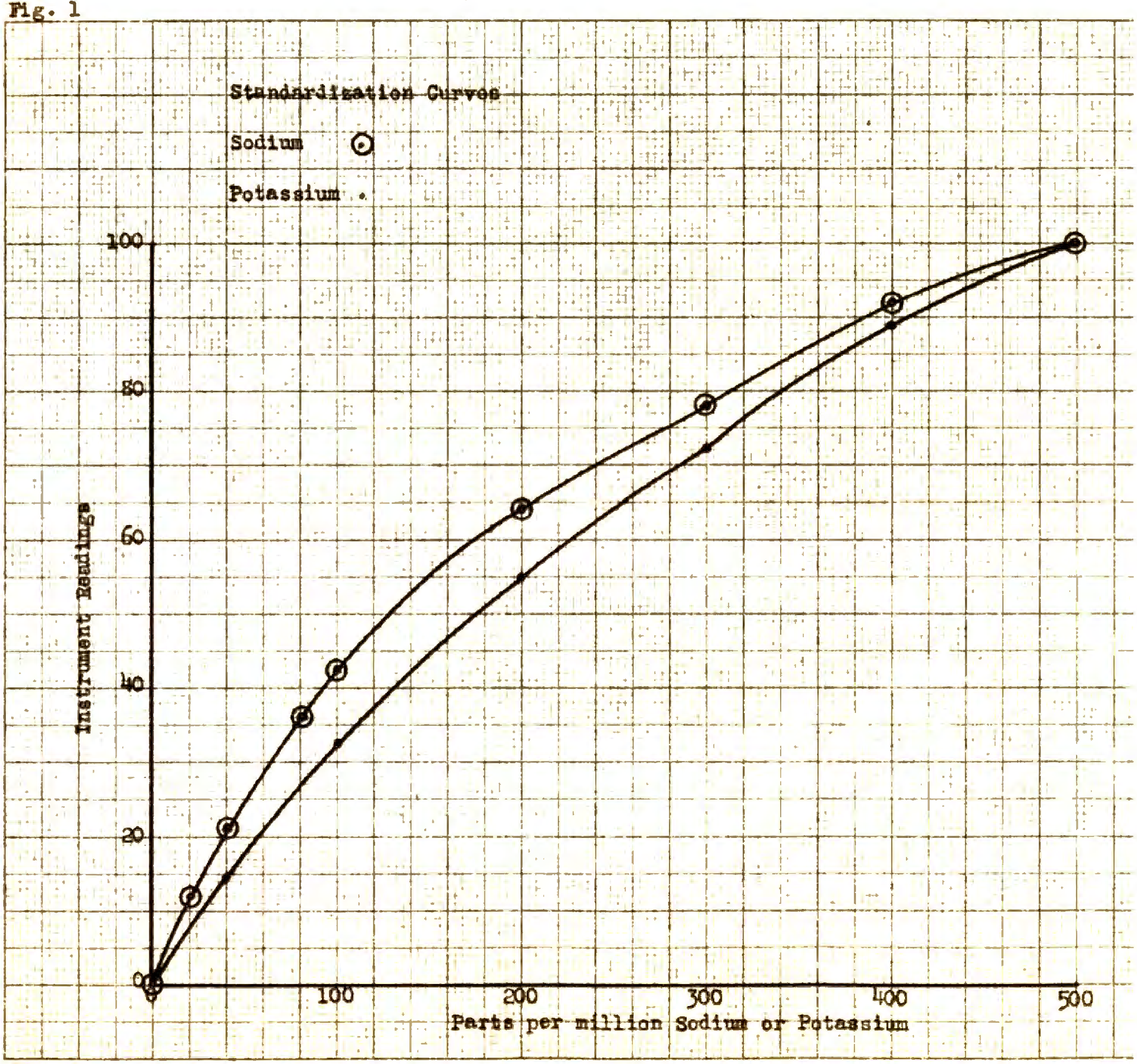

Standardization Curves
Sodium ⊙
Potassium •
Instrument Readings
0
20
40
60
80
100
0
100
200
300
400
500
Parts per million Sodium or Potassium

Fig. 1

Fig. 2

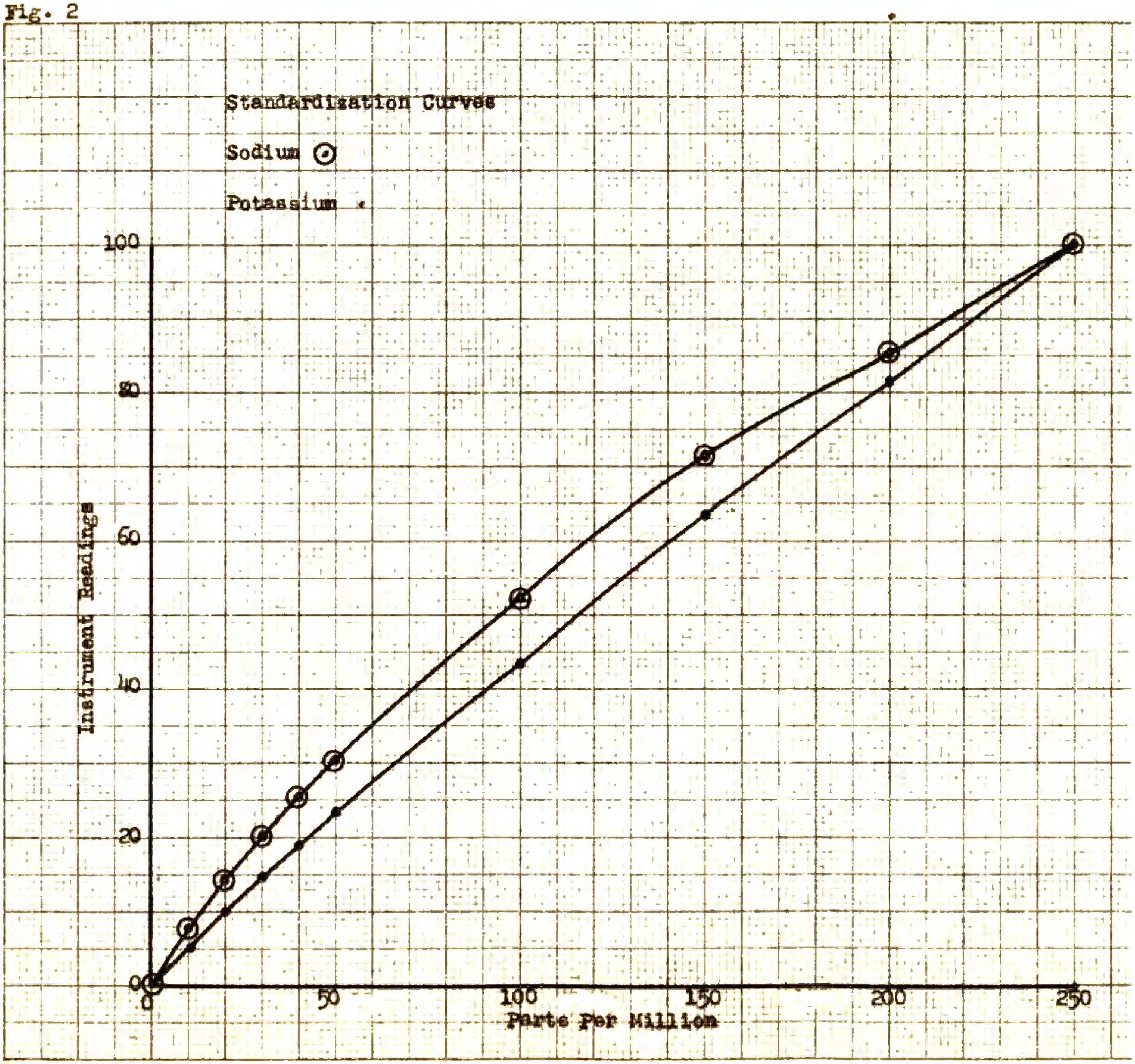
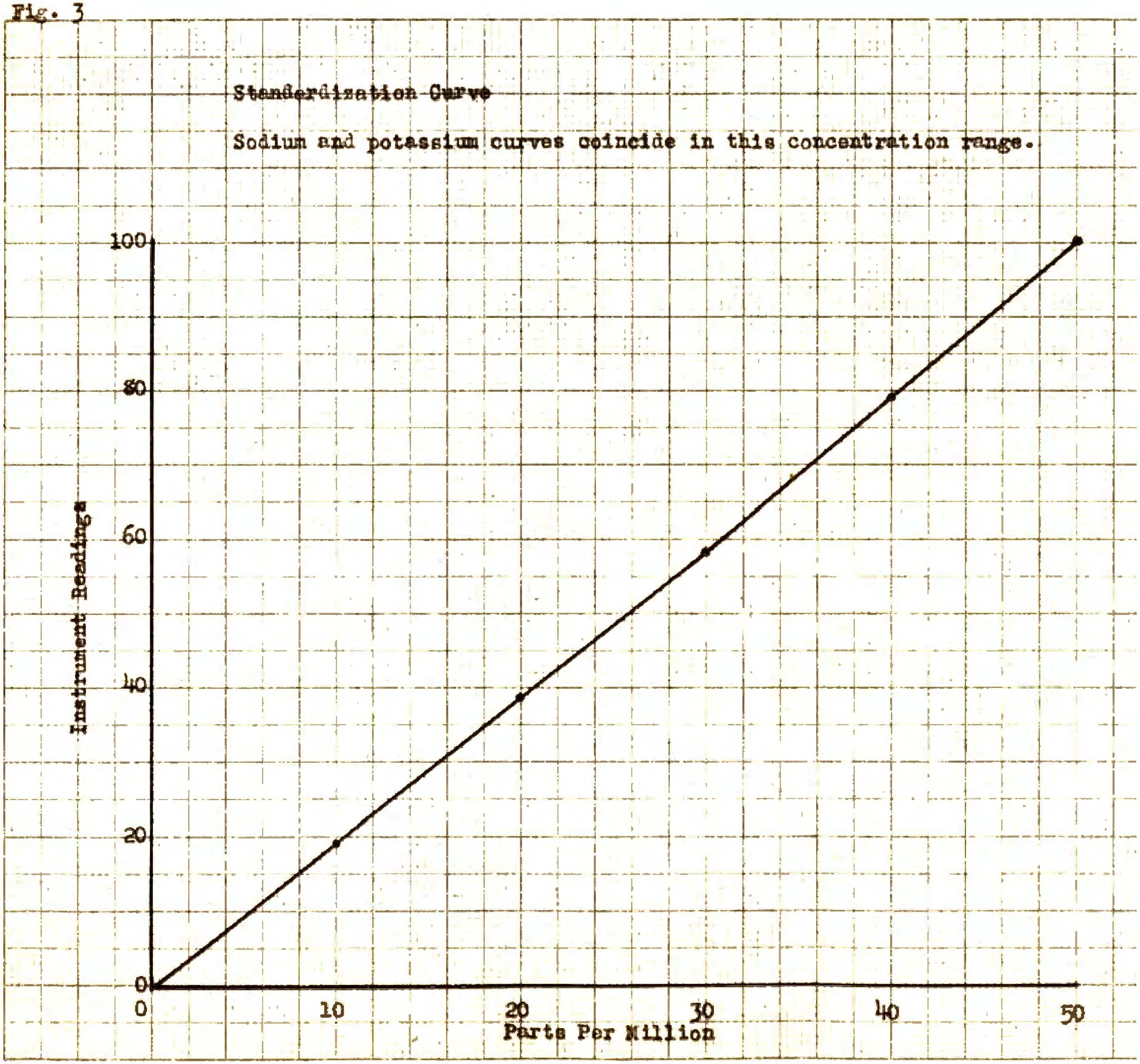

Standardization Curves
Sodium ⊙
Potassium •
Instrument Readings
100
80
60
40
20
0
0
50
100
150
200
250
Parts Per Million

Fig. 2

Fig. 3



Standardization Curve

Sodium and potassium curves coincide in this concentration range.

Fig. 3

KIND OF FUEL, PRESSURE OF AIR AND GAS, GAS JET SIZE, FLOW THROUGH ATOMIZER, ETC.

Air pressure, gas pressure, gas and air mixture in the burner, and amount of solution used are so interrelated that it seems best to discuss these topics as a unit. Ordinary city gas is not dependable because neither the pressure nor the composition is constant. In this investigation commercial bottled butane was used with two pressure regulators in the line. No other fuels were tried, but among those which have been suggested are hydrogen, propane, and acetylene.

The air inlet of the burner is not adjustable so the only way to change the proportion of air and gas in the burner is to change the speed of the gas passing through the gas jet by changing the gas pressure, or by varying the size of the orfice through which the gas enters the burner tube. The gas jet is removable; consequently, gas jets of several sizes were made so that the amount and velocity of the gas could be varied. As in any gas burner, a blue flame can be obtained by using the proper gas and air mixture. A blue flame, without any yellow cap, is absolutely necessary in the operation of this instrument because the yellows and reds in such a flame are important components of the spectra of sodium and potassium. Feeding a spray of liquid into the flame cools the flame and tends to produce the yellow flame; therefore, the gas and air mixture must be so adjusted as to maintain a blue flame with the normal amount of liquid passing through it.

The proper air pressure for the atomizer had to be determined. It was found that if the air pressure was too low, the solution was broken up into large droplets, very few of which were drawn into the burner. If the pressure was too high, too much solution was fed into the flame which caused the yellow flame mentioned above. In addition there is the possibility that more mist may be formed than the burner can draw in so the total solution will not be analyzed. The proper settings for some of these factors were obtained by the trial and error method and the observations leading to the proper settings were not easily recorded. For example, the gas pressure and jet size were set to give the proper flame with a certain air pressure on the atomizer. Then, for other reasons it was decided that a different air pressure would be better. As soon as use was made of the different air pressure, consistent readings could not be obtained because the flame was yellow; consequently, the next job was to change the gas jet and gas pressure so as to get the proper flame at the new air pressure. The results obtained by using different air pressure and different gas pressures with a given gas jet are shown by Fig's. 4 - 9.

These graphs are very irregular. A similar sort of irregularity is shown by Cholak and Hubbard[1] in using an air and acetylene flame.

The following settings were finally decided upon as giving the best results with the instrument: Gas pressure equal to 17-18 inches of water, gas jet orfice equal to .013 inch in diameter (standard twist drill No. 80), and an air pressure of 11 pounds per square inch.

The air compressor that was used was set to turn on at 20 pounds and turn off at 35 pounds. Working with this variation it was found that the regulator on the instrument did not maintain a very constant pressure on the atomizer; therefore, a second pressure regulator set at 17 pounds was used in the line. With this arrangement the pressure was held to an accuracy of plus or minus one quarter of a pound. No attempt was made to hold the air pressure

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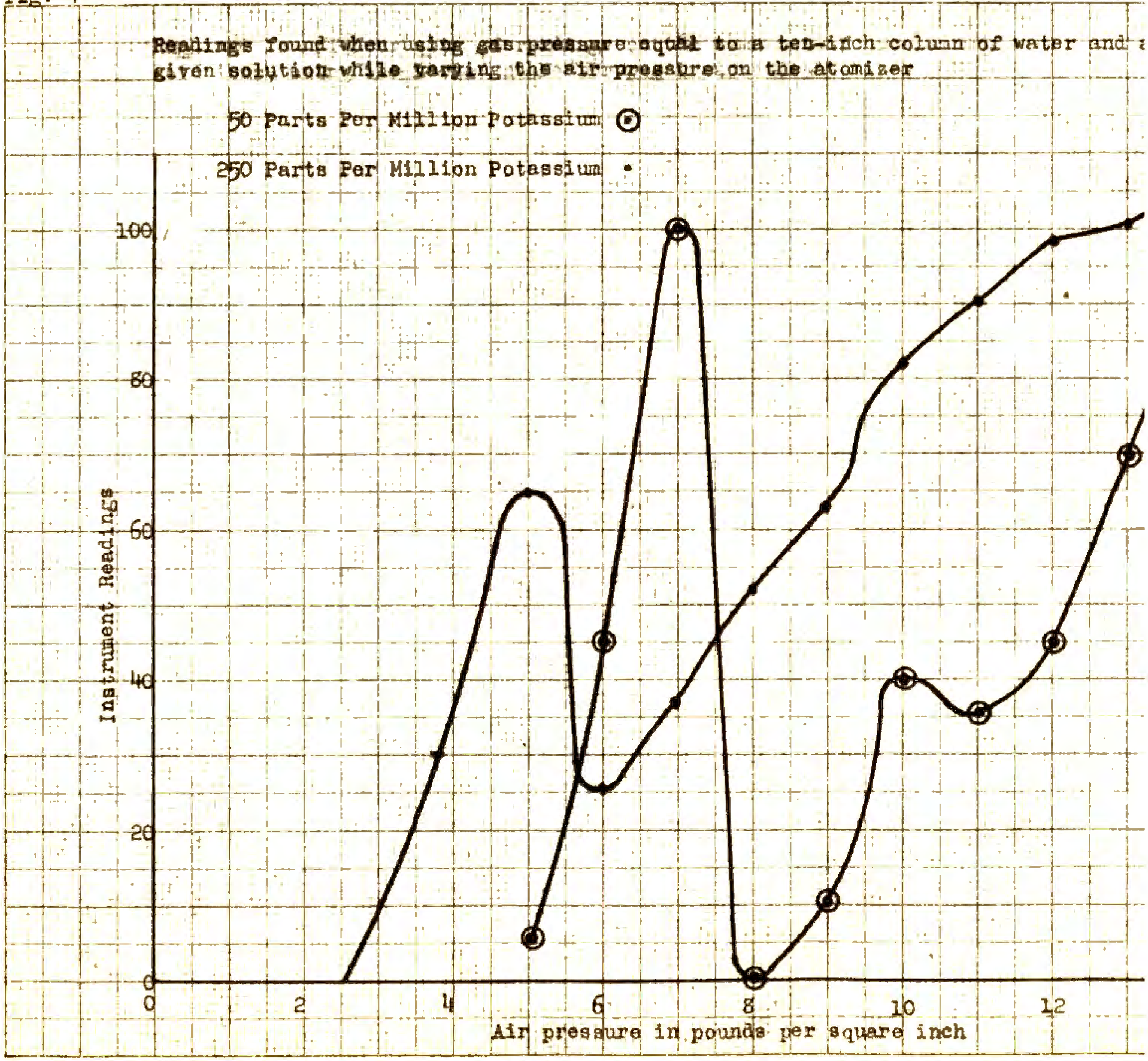
[1] Cholak, J., and Hubbard, D. M., <u>Ind</u>. <u>Eng</u>. <u>Chem</u>., <u>Anal</u>. <u>Ed</u>. 16, pp. 728-34 (1944).

Fig. 4

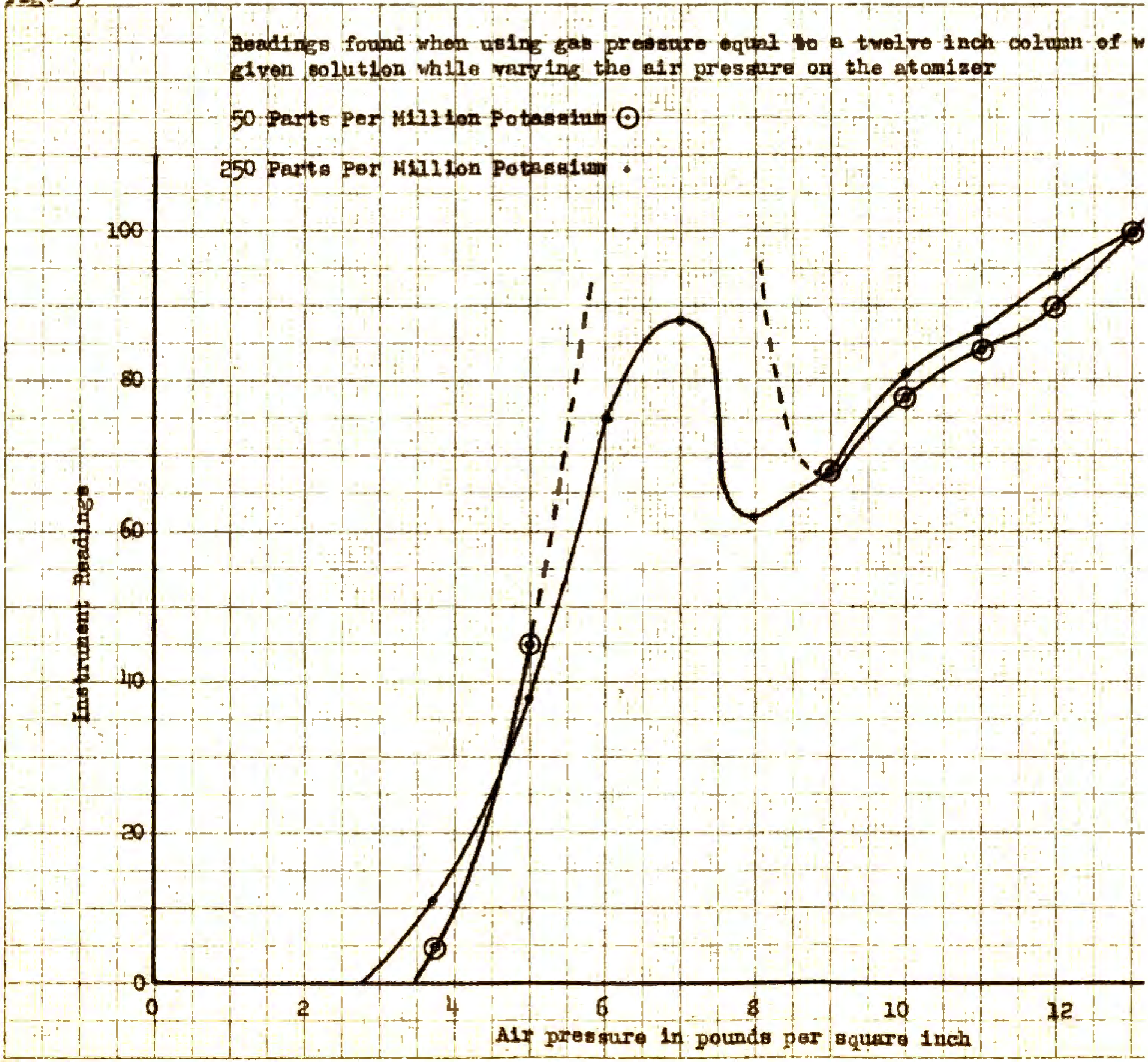


Readings found when using gas pressure equal to a ten-inch column of water and

given solution while varying the air pressure on the atomizer

Fig. 4

Fig. 5



Readings found when using gas pressure equal to a twelve inch column of w
given solution while varying the air pressure on the atomizer

50 Parts Per Million Potassium ⊙

250 Parts Per Million Potassium •

Fig. 5

Fig. 6

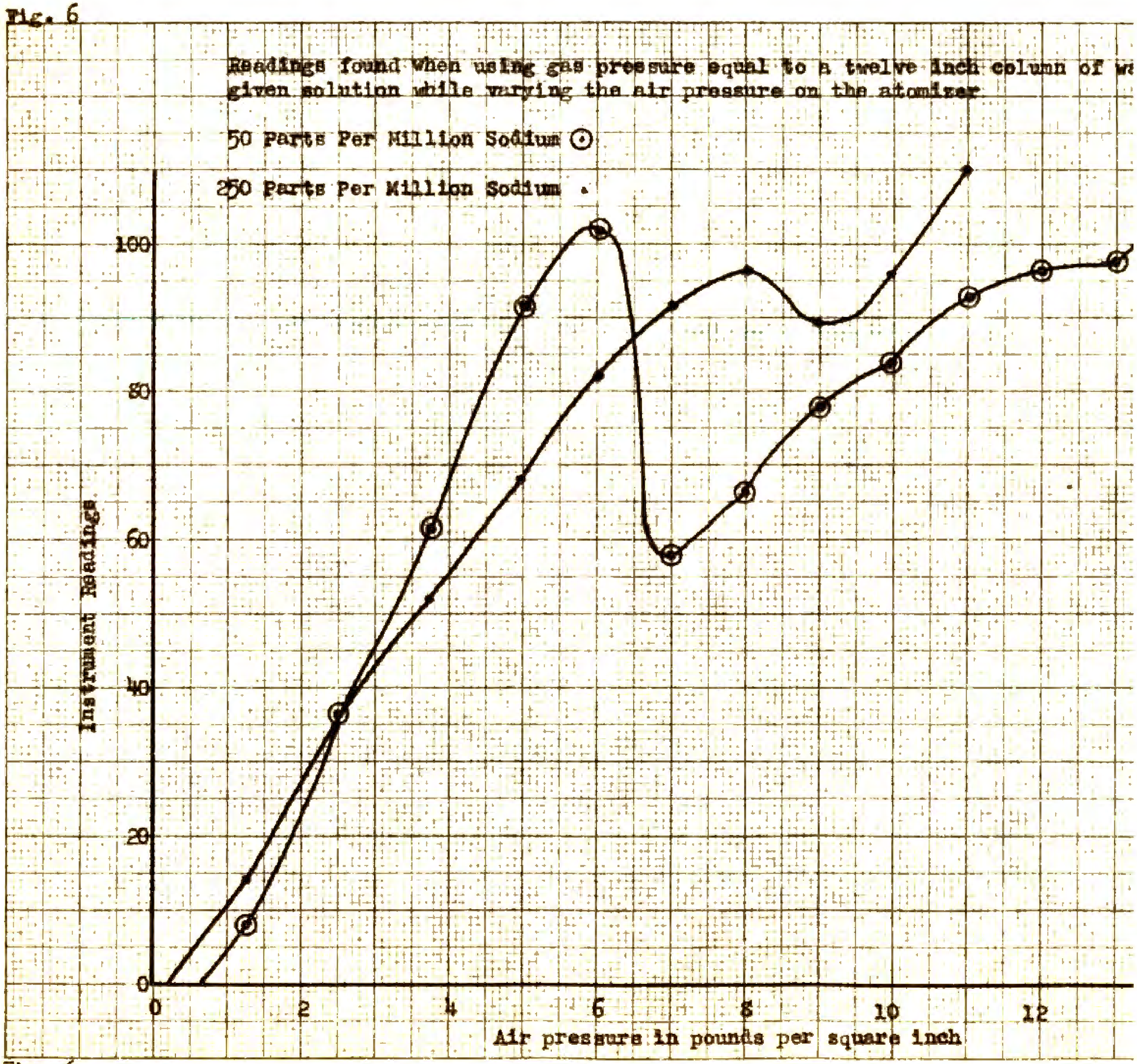

Readings found when using gas pressure equal to a twelve inch column of wa
given solution while varying the air pressure on the atomizer
50 Parts Per Million Sodium ⊙
250 Parts Per Million Sodium •
Instrument Readings
0
20
40
60
80
100
0
2
4
6
8
10
12
Air pressure in pounds per square inch

Fig. 6

Fig. 7

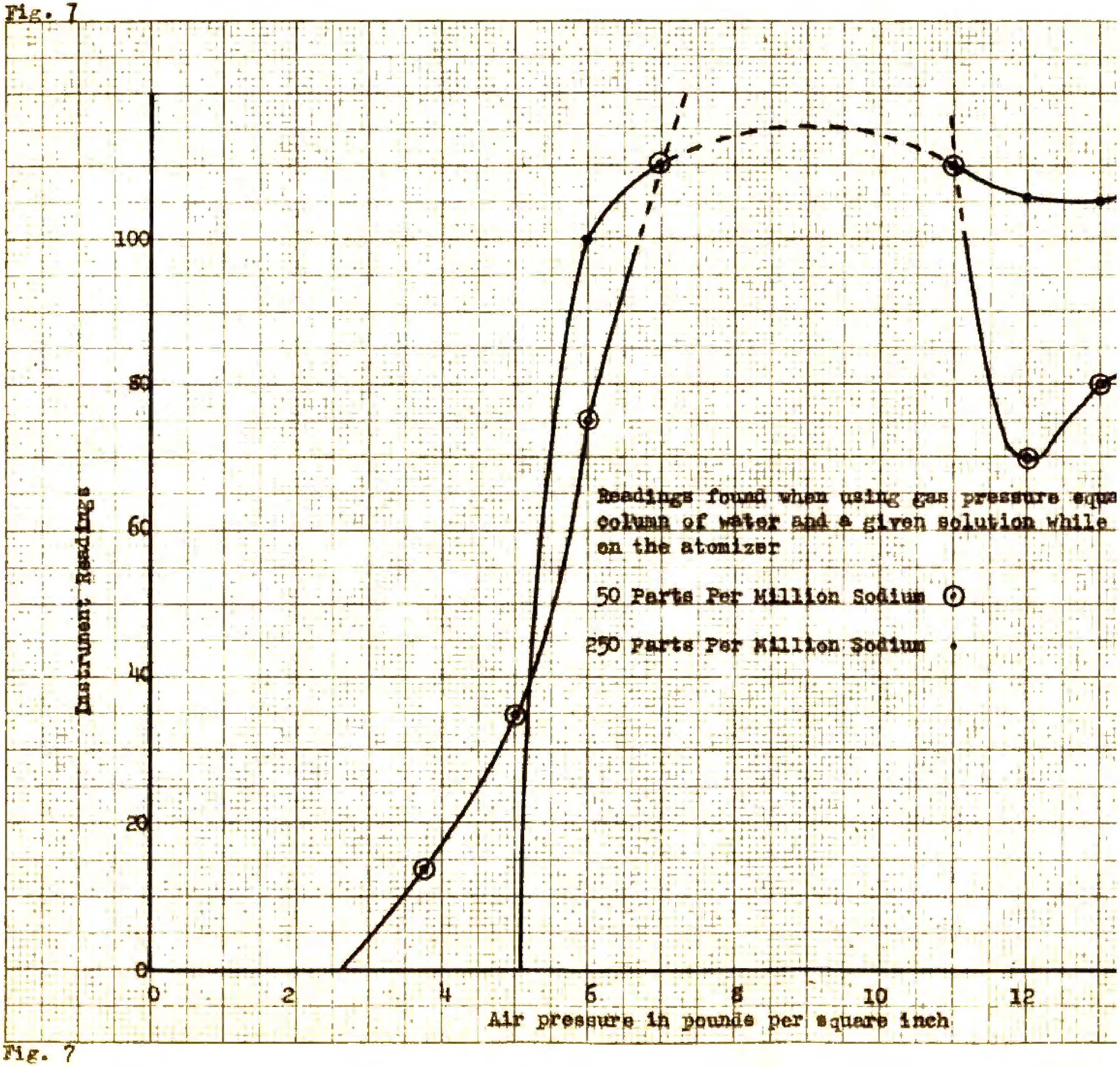
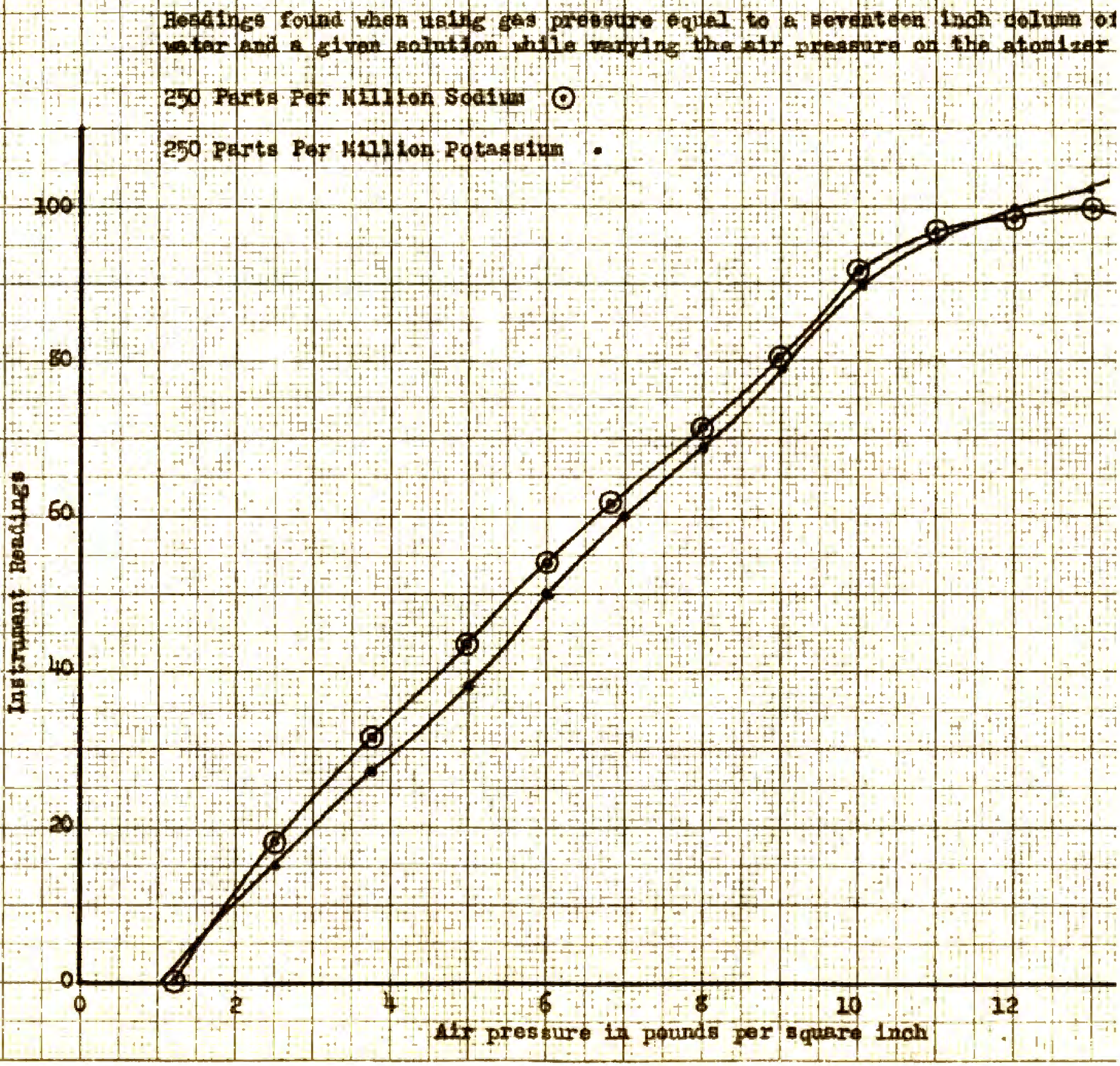

Instrument Readings
100
80
60
40
20
0
0
2
4
6
8
10
12
Air pressure in pounds per square inch
Readings found when using gas pressure equ
column of water and a given solution while
on the atomizer
50 Parts Per Million Sodium ⊙
250 Parts Per Million Sodium •

Fig. 7

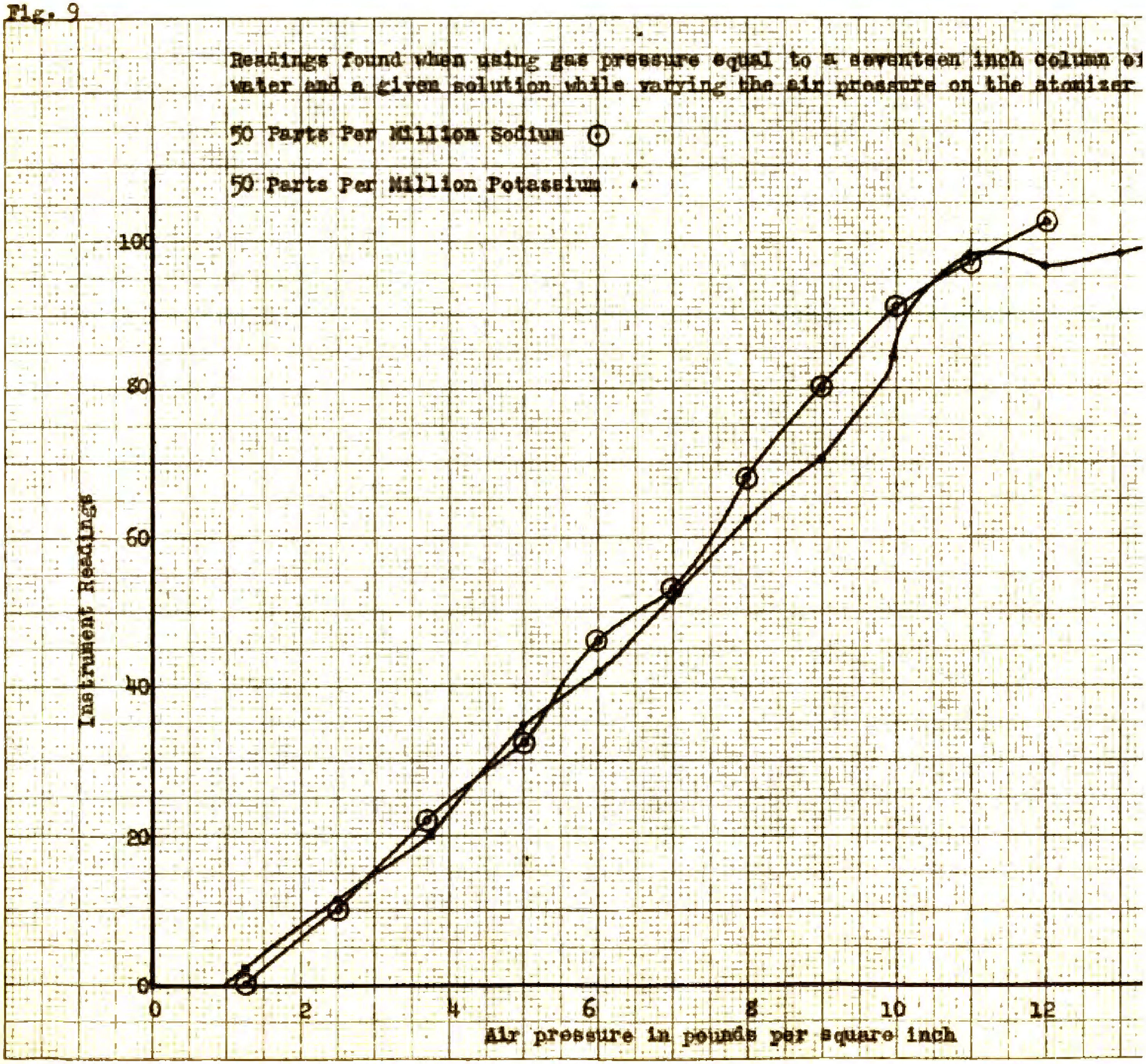
Fig. 8



Readings found when using gas pressure equal to a seventeen inch column of water and a given solution while varying the air pressure on the atomizer

Fig. 8

Fig. 9



Readings found when using gas pressure equal to a seventeen inch column of water and a given solution while varying the air pressure on the atomizer

Fig. 9

to closer limits. In view of the statement by Rauterberg and Knippenberg[2] concerning their instrument, that a drop of .02 atmosphere in the pressure causes an error of .5%, it is possible that the accuracy of the flame photometer might be improved by more precise control of the air pressure. To remove dust from the air, the air was filtered through glass wool moistened with S.A.E. No. 40 motor oil.

When the instrument is properly warmed up and standardized for potassium determination, a puff of tobacco smoke blown into the burner compartment will cause the instrument to indicate a considerable amount of potassium. Potassium determinations made when there is an appreciable amount of tobacco smoke in the room cannot be accepted. Tobacco smoke does not seem to effect sodium analysis.

The solution is drawn to the atomizer through a capillary tube. Since substances dissolved in water change its surface tension and viscosity and since the rate of flow of liquid through the capillary would be dependent upon these two, it might be expected that solutions of varying compositions might flow through the tube at different rates. The rate of flow of various solutions with concentrations of sodium and potassium ranging from 0 to 500 parts per million was timed, but no indication was found of any change in rate of flow caused by changes in concentration in this range.

The capillary tube is essentially in the form of an inverted U so there is the possibility of siphon action partially determining the rate of flow. The container used for the solution was a standard 50 ml. beaker. The maximum variation of head on the siphon would be the height of the beaker. To determine the difference in rate of flow when the beaker was full and when it

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[2] Rauterberg, E., and Knippenberg, E., <u>Ernahr Pflanze</u> 37, pp. 73-6 (1941).

was nearly empty, the time to drain the last 25 ml. from the beaker was recorded and also the time to drain a full 50 ml. from the beaker. The average rate of flow obtained in the first case would be the rate of flow when the beaker was one-fourth full. The rate found by using the difference of the two times would be the rate when the beaker is three-fourths full. Fig. 10 is based on these observations. The change is not great but it is suggested that the beaker be kept above three-fourths full while running any analysis. It is to be noted that these measurements were made with two atomizers. Atomizer No. 1 was the atomizer originally furnished with the instrument. Atomizer No. 3 was a spare atomizer bought from the Perkin Elmer Corporation. The great difference in performance between the two atomizers should be noted. It is not known whether the second atomizer represents a chance defective piece of material, or represents a true picture of the tolerance allowed by the company in making of spare parts. All other measurements recorded in this report were made using atomizer No. 1.

The gas meter available in this investigation was not considered too accurate. The measurements made indicate that the atomizer working at 11 pounds per square inch pressure will not use in excess of one-half cubic foot of air per minute (volume measured at atmospheric pressure). The burner probably will not use in excess of 2.5 cubic feet of butane per hour, using a burner jet .013 inch in diameter and a pressure of atmospheric pressure plus a pressure equal to a 17.75-inch column of water (butane measured at the mentioned working pressure).

Fig. 10

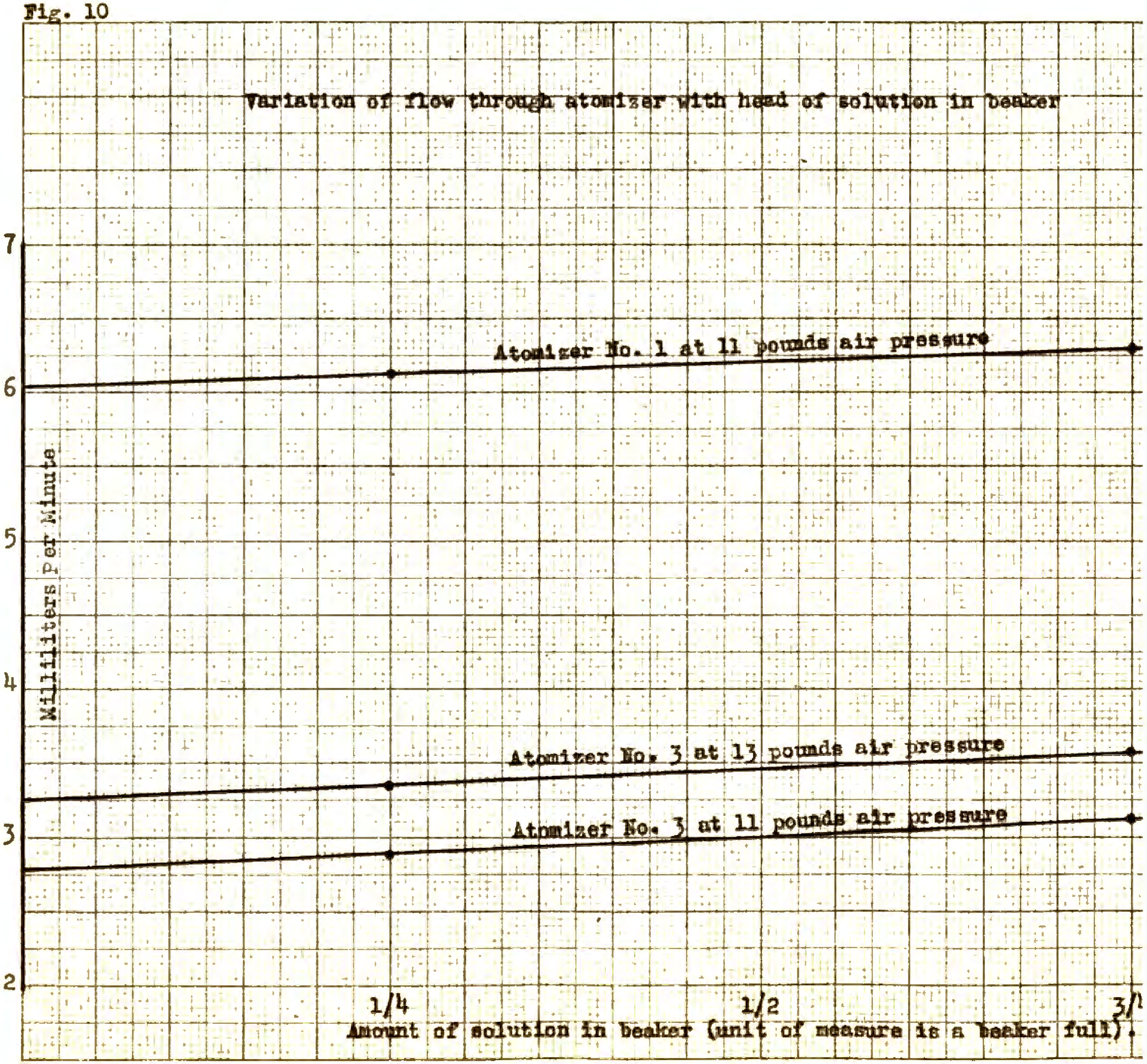

Variation of flow through atomizer with head of solution in beaker
Atomizer No. 1 at 11 pounds air pressure
Atomizer No. 3 at 13 pounds air pressure
Atomizer No. 3 at 11 pounds air pressure
Milliliters Per Minute
7
6
5
4
3
2
1/4
1/2
3/
Amount of solution in beaker (unit of measure is a beaker full).

Fig. 10

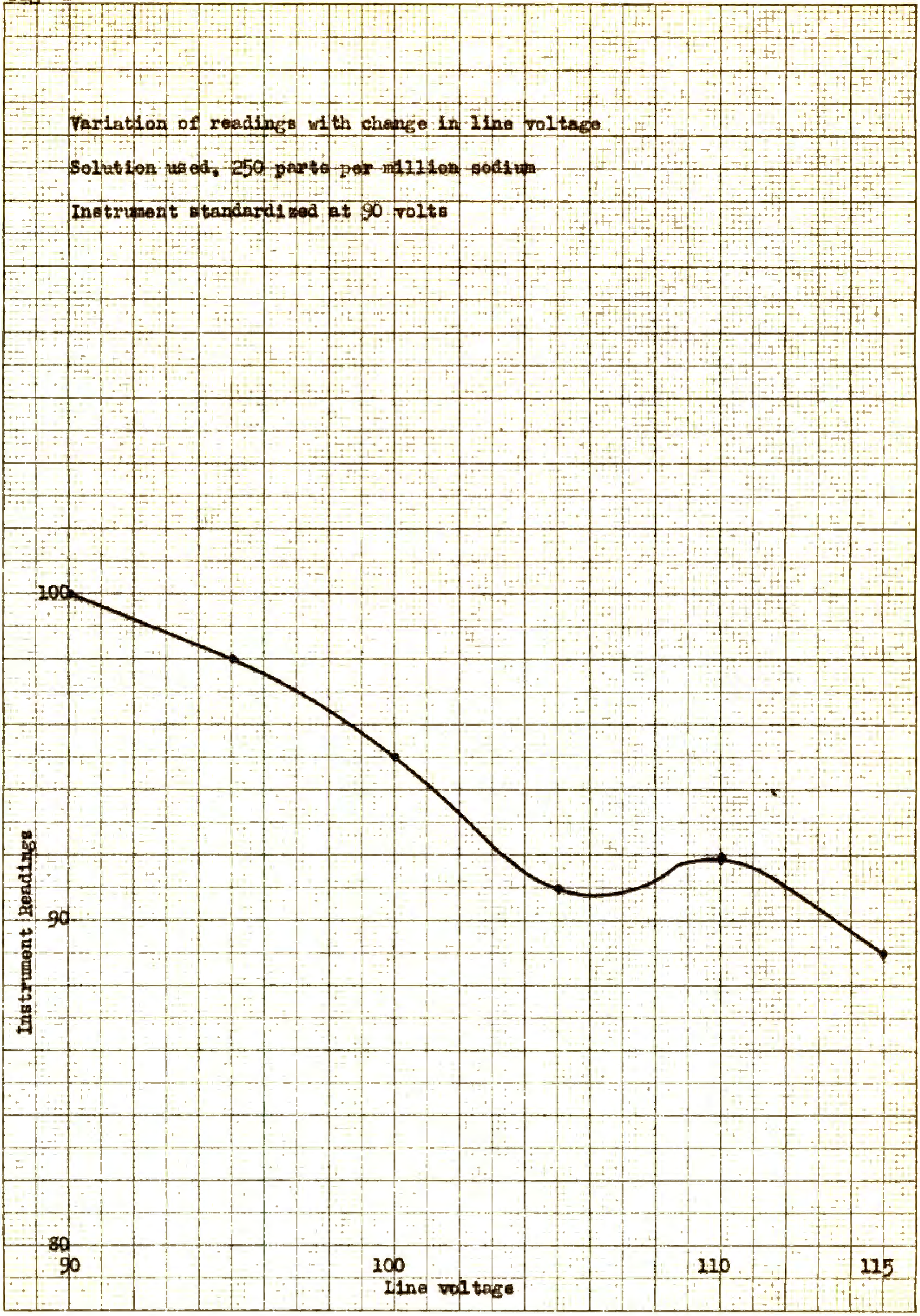
FLUCTUATION OF LINE VOLTAGE

Fig. 11 shows the variation of readings due to fluctuations in line voltage. These figures were obtained by connecting a "Varitran" in the line to the instrument and varying the voltage while using the same solution. This graph shows that the readings between 104 and 112 volts do not vary more than one-half percent from the average in that interval. On the other hand, the error increases rapidly below 104 volts. It is also to be noted from the graph that the readings increase as the voltage decreases.

FATIGUE OF PHOTO-CELLS

Photo-cells are subject to fatigue. The manufacturer recommends that the instrument be warmed up for one-half hour before operation. In practice, however, much more consistent readings were obtained by allowing a full hour for warm-up. Even after an hour the standard settings vary slightly (the zero setting varying more than the high standard setting) so the zero and high standard settings should be re-checked at least every half hour. When changing from sodium to potassium or vice versa the hour warm-up is also necessary. In operation one should arrange to work on one metal for a half day at a time. To one unaccustomed to the instrument this time for warm-up and re-checking may seem excessive; however, if one uses the warm-up hour to arrange samples and keep records one can take at least 150 readings in an eight-hour day.

Fig. 11



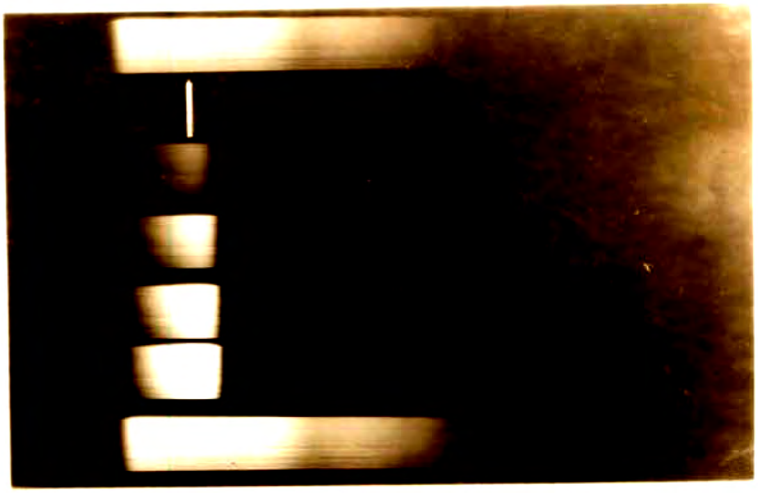
Variation of readings with change in line voltage

Solution used, 250 parts per million sodium

Instrument standardized at 90 volts

CHARACTERISTICS OF LIGHT FILTERS

To determine the characteristics of the light filters in the flame photometer, use was made of a transmission grating spectrograph.



In the above picture, the top and bottom bands, is shown a continuous first order spectrum of a 200-watt incandescent light to the limit of sensitivity of the film used (Arrow Pan, emulsion No. 6496-7106). Second from the top is the sodium D-Doublet Line. To obtain the other four spectra shown, the light filters used for sodium determination in the flame photometer were placed directly in front of the spectrograph slit and the 200-watt incandescent bulb was used with exposure times of 1, 5, 10, and 20 seconds respectively.

An attempt was made to make the same kind of spectrographic picture using the light filters from the potassium side of the flame photometer. In this case no transmission was detected in the range of sensitivity of the film, even at 20 seconds exposure. These observations seem to indicate that, (1) the instrument measures sodium on the intensity of the sodium D-Line, (2) the instrument probably measures potassium on the intensity of the lines at 7664.94 and 7699.01 A°, and (3) the filters used for potassium successfully block out the sodium D-Lines - and probably vice versa.

INTERFERING ELEMENTS

Sodium chloride, carbonate, bicarbonate, and sulfate standard solutions were made and run on the instrument. These four acid radicals caused no measurable difference in the determination of the sodium content. All other metal solutions used in this research were made up from chlorides of the metal. (All standard solutions used in this research were made up from well known brands of reagent grade chemicals).

In determining the interference caused by other metals two sets of observations were run. Solutions of 5,000 parts per million of the metals listed in Table I were made up and run on the instrument against 50 part per million standards. These gave readings indicating apparent parts per million of the element used as standard, as shown in Table I.

TABLE I

Metal	50 P.P.M. Na Standard	50 P.P.M. K Standard
Li	13.5	.75
Mn	1.0	3.5
Fe	4.5	3.0
Ca	24.5	7.5
Mg	0.0	.75
Co	3.0	5.0
Sr	26.0	1.25
Ba	3.5	43.0
Cu	1.0	1.0
K	4.5	-
Na	-	6.0
Th	5.0	3.0
Cs	45.0	3.3

A series of solutions of mixtures of sodium, potassium, and an interfering metal was made. Concentrations of sodium and potassium were 200, 100, 50, and 20 parts per million and concentrations of the other metal were 500, 100, and 50 parts per million. Table II gives the instrument readings on these solutions when run against 250 part per million standards.

TABLE II

	500 p.p.m. Fe	100 p.p.m. Fe	50 p.p.m. Fe	Zero p.p.m. Fe
200 p.p.m. Na	80.2	86.3	88.0	85.0
100 p.p.m. Na	47.5	53.0	54.3	52.25
50 p.p.m. Na	26.7	30.3	31.0	30.5
20 p.p.m. Na	12.8	14.0	14.7	14.0
200 p.p.m. K	73.0	83.5	84.5	81.25
100 p.p.m. K	40.0	46.0	47.25	43.5
50 p.p.m. K	20.5	23.75	24.0	22.75
20 p.p.m. K	8.25	9.25	9.5	8.75

	500 p.p.m. Ca	100 p.p.m. Ca	50 p.p.m. Ca	Zero p.p.m. Ca
200 p.p.m. Na	84.5	85.0	85.0	85.0
100 p.p.m. Na	52.0	51.5	50.5	52.25
50 p.p.m. Na	29.0	29.0	29.0	30.5
20 p.p.m. Na	14.0	13.5	13.5	14.0
200 p.p.m. K	74.0	82.25	83.0	81.25
100 p.p.m. K	42.25	44.0	44.5	43.5
50 p.p.m. K	21.25	22.25	22.75	22.75
20 p.p.m. K	9.25	9.5	9.5	8.75

	500 p.p.m. Mg	100 p.p.m. Mg	50 p.p.m. Mg	Zero p.p.m. Mg
200 p.p.m. Na	78.25	80.5	84.5	85.0
100 p.p.m. Na	46.0	51.25	50.75	52.25
50 p.p.m. Na	25.25	28.25	28.5	30.5
20 p.p.m. Na	11.75	12.25	12.25	14.0
200 p.p.m. K	72.5	77.0	79.0	85.0
100 p.p.m. K	41.5	42.5	43.5	43.5
50 p.p.m. K	20.5	24.25	24.0	22.75
20 p.p.m. K	11.5	10.5	10.75	8.75

	500 p.p.m. Ba	100 p.p.m. Ba	50 p.p.m. Ba	Zero p.p.m. Ba
200 p.p.m. Na	85.25	85.5	85.5	85.0
100 p.p.m. Na	51.5	53.25	53.25	52.25
50 p.p.m. Na	30.5	31.5	31.5	30.5
20 p.p.m. Na	14.25	14.25	15.0	14.0
200 p.p.m. K	77.5	73.75	74.0	85.0
100 p.p.m. K	40.5	41.5	41.5	43.5
50 p.p.m. K	22.5	23.0	23.5	22.75
20 p.p.m. K	10.0	9.0	10.0	8.75

TABLE II (Continued)

	500 p.p.m. Li	100 p.p.m. Li	50 p.p.m. Li	Zero p.p.m. Li
200 p.p.m. Na	78.5	82.5	83.5	85.0
100 p.p.m. Na	47.25	50.5	50.5	52.25
50 p.p.m. Na	24.75	28.0	27.75	30.5
20 p.p.m. Na	12.0	12.5	12.25	14.0
200 p.p.m. K	69.0	74.5	77.5	85.0
100 p.p.m. K	38.5	41.5	43.0	43.5
50 p.p.m. K	17.75	21.75	21.5	22.75
20 p.p.m. K	7.0	8.0	8.25	8.75

	500 p.p.m. Mn	100 p.p.m. Mn	50 p.p.m. Mn	Zero p.p.m. Mn
200 p.p.m. Na	85.75	86.25	87.0	85.0
100 p.p.m. Na	53.5	53.5	54.75	52.25
50 p.p.m. Na	28.75	29.75	31.0	30.5
20 p.p.m. Na	12.5	13.25	13.5	14.0
200 p.p.m. K	78.5	84.0	81.0	85.0
100 p.p.m. K	42.0	44.0	44.0	43.5
50 p.p.m. K	15.0	15.0	14.0	22.75
20 p.p.m. K	6.0	7.0	6.0	8.75

These observations indicate that barium, strontium, calcium, and lithium cause considerable interference in the use of the flame photometer, and some of the other elements interfere to a lesser degree. This seems to be in accord with the findings of Parks, Johnson and Lykken[1] who made the following statement concerning their findings on this same model of instrument:

> "The flame photometer method has proven useful for the rapid determination of sodium and potassium in solutions of restricted composition, but it has been found that serious errors are sometimes caused by the interfering action of certain common substances in the test solution. Very large negative errors are caused by appreciable concentrations of phosphate, borate, and oxalate ions and by very high concentrations of mineral acids; large positive errors are found with alcohol and acetic acid. Moderate to large errors for sodium and/or potassium are produced by ammonium, alkali, alkaline earth, and other cations, particularly when these are present in high concentrations. Occasionally, compensating errors are realized."

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[1] Parks, T. D., Johnson, H. O., Lykken, L., "Interferences in the Determination of Alkali Metals by Flame Photometry," Monograph P-32, Shell Development Company, Emeryville, California.

It is recommended that anyone wishing to use the flame photometer in routine analyses on one particular type of samples, should first determine the general nature of that type of sample and determine the amount of error it will cause on this instrument. It could then be decided whether the accuracy falls within their requirements, or whether certain substances should be removed from the samples before making use of the flame photometer.

ACCURACY

In an effort to determine the reproducibility of instrument readings and to determine the sensitivity of the galvanometer built into the instrument, the following procedure was followed: A more sensitive galvanometer having an internal resistance of approximately 1,150 ohms (Leeds and Northrup, Model No. 2310), hereinafter to be referred to as the Leeds and Northrup galvanometer, was connected into the instrument circuit through a double pole, double throw switch in such a way as to allow the operator to use either the built-in galvanometer or the Leeds and Northrup galvanometer at will. The Leeds and Northrup galvanometer may be seen sitting to the left of the flame photometer in the picture on Page 5. Also, wired into the circuit to the Leeds and Northrup galvanometer was used an assembled resistance coil having a total resistance of approximately 6,500 ohms, and being divided into 9 approximately equal parts by the use of a total of 10 taps on the coil. This coil was used as a combination resistance and shunt to enable the operator to vary the sensitivity of the Leeds and Northrup galvanometer (wiring diagram in Fig. 12). A series of solutions of sodium of varying concentrations and also a similar series of solutions of potassium were prepared. Each series was run four times using the built-in galvanometer, and four times using the Leeds and Northrup galvanometer. The first two of each four were run starting with the most concentrated solution and working down to least concentrated one. The other two runs were made in reverse order. The results are listed in Table III.

Fig. 12

WIRING FROM LEEDS AND NORTHRUP GALVANOMETER TO FLAME PHOTOMETER

G1 Original Galvanometer
A1 and A2 Leads to Photo-Cell Circuit
S Double Pole, Double Throw Switch
R Resistance Coil (total resistance approximately 6,500 ohms, 10 taps)
G2 Leeds and Northrup Galvanometer (Model No. 2310)

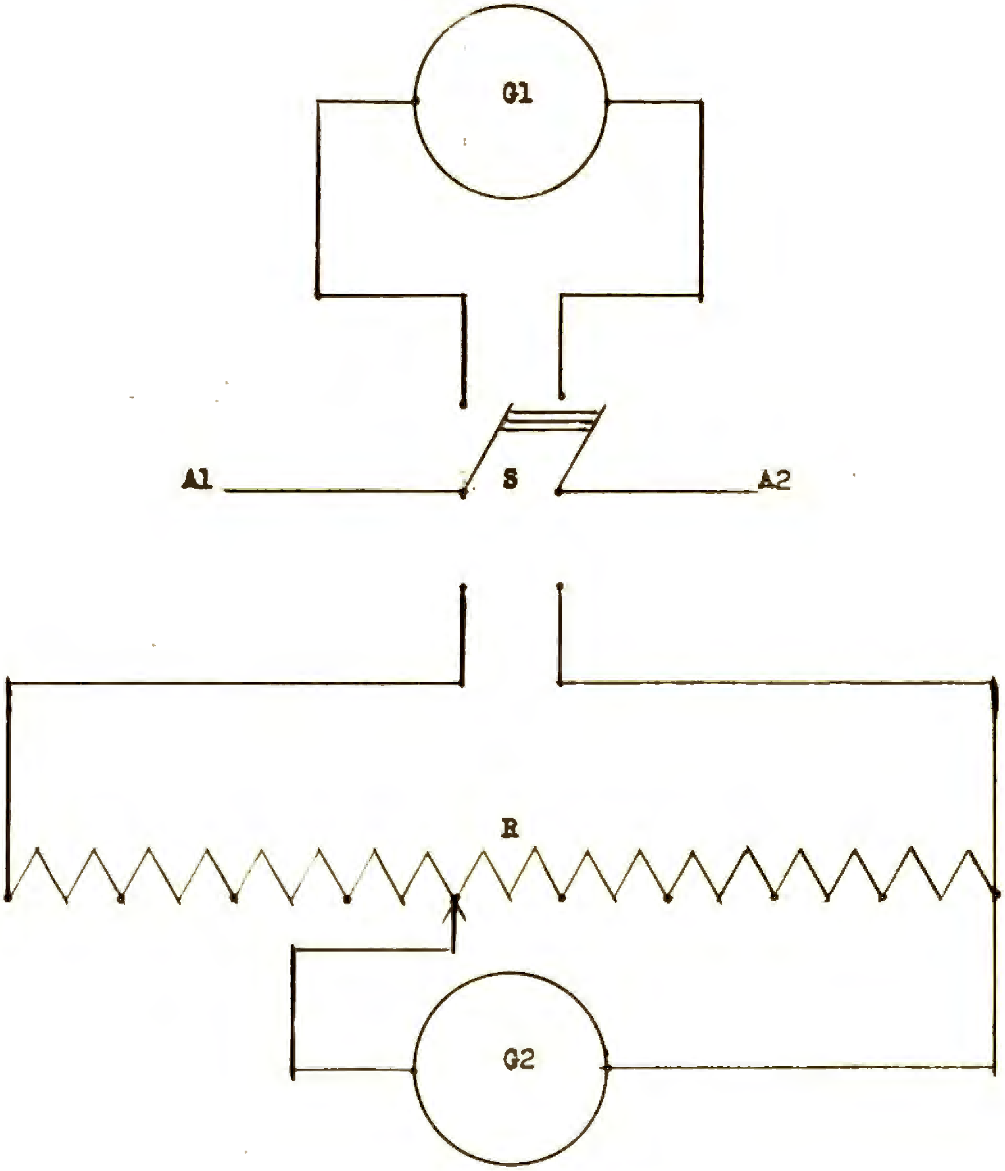


TABLE III

INSTRUMENT READINGS

P.P.M.	1st.	2nd.	3rd.	4th.	Average	Maximum Deviation	Percent Deviation
Built-in Galvanometer - 5,000 p.p.m. Na used as high standard							
5,000	100.0	100.0	95.0	98.0	98.25	3.25	3.3
4,000	82.0	81.0	78.0	79.0	80.0	2.0	2.5
3,000	72.0	72.0	71.0	70.0	71.25	1.25	1.8
2,000	64.0	64.0	62.0	61.0	62.75	1.75	2.8
1,000	50.0	47.0	47.0	47.0	47.75	.75	1.6
500	31.0	29.0	29.0	29.0	29.5	1.5	5.1
400	27.0	26.0	26.0	24.0	25.75	1.75	6.8
300	23.0	22.0	21.0	21.0	21.75	1.25	5.7
200	19.0	16.75	16.0	16.0	16.9	2.1	12.4
100	13.0	10.5	9.75	9.75	10.75	1.25	11.6
90	12.0	9.75	8.75	9.5	10.0	2.0	20.0
80	11.0	8.5	8.0	8.25	8.9	2.1	23.6
70	10.0	7.75	7.0	7.25	8.0	2.0	25.0
60	9.0	7.0	6.0	6.0	7.0	2.0	28.6
50	9.0	5.75	4.75	5.25	6.2	2.8	45.2
45	8.75	5.25	4.25	4.75	5.75	3.0	52.2
40	8.25	4.75	4.0	4.5	5.4	2.85	52.8
35	7.25	4.0	3.5	3.75	4.6	2.65	57.6
30	6.25	3.75	3.0	3.25	4.1	2.15	52.4
25	5.75	3.5	2.5	3.0	3.7	2.05	55.4
20	5.25	3.0	1.75	2.5	3.1	2.15	69.4
15	4.75	2.25	1.0	1.5	2.8	1.95	69.6
10	4.5	1.25	.75	1.0	1.9	2.6	137.0
5	3.75	.75	.5	1.25	1.6	2.15	156.0
0	3.5	.5	.0	.0	1.0	2.5	250.0
Built-in Galvanometer - 500 p.p.m. Na used as high standard							
500	100.0	100.0	103.0	98.0	100.25	2.75	2.8
400	85.0	89.0	88.0	85.0	86.75	2.25	2.6
300	74.0	74.0	74.0	71.0	73.25	2.25	3.1
200	58.0	59.0	56.0	56.0	57.25	1.75	3.1
100	36.0	36.0	32.0	34.0	34.5	2.5	7.2
90	33.0	33.0	30.0	31.0	31.75	1.75	5.5
80	29.0	30.0	27.0	29.0	28.75	1.75	6.1
70	27.0	28.0	24.0	26.0	26.25	2.25	8.6
60	24.0	25.5	21.0	22.0	23.13	2.13	9.2
50	20.0	22.0	17.0	18.0	19.25	2.75	14.3
45	18.0	19.0	15.0	16.25	17.06	2.06	12.1
40	18.0	18.25	14.0	14.5	16.19	2.19	13.5
35	15.0	16.0	12.0	13.0	14.0	2.0	14.3
30	14.0	14.0	10.5	11.5	12.5	2.0	16.0
25	12.0	12.5	9.0	10.0	10.9	1.9	17.4
20	10.0	11.0	7.5	9.25	9.44	1.94	20.5

TABLE III (Continued)

INSTRUMENT READINGS

P.P.M.	1st.	2nd.	3rd.	4th.	Average	Maximum Deviation	Percent Deviation
Built-in Galvanometer - 500 p.p.m. Na used as high standard (Continued)							
15	8.75	8.75	6.5	5.25	7.31	2.06	28.2
10	6.75	6.0	4.25	4.5	5.37	1.38	25.7
5	4.5	4.0	3.0	4.75	4.06	1.06	26.1
0	3.5	1.0	0.0	0.0	1.12	2.38	212.5
Built-in Galvanometer - 50 p.p.m. Na used as high standard							
50	100.0	100.0	104.0	105.0	102.25	2.75	2.69
45	84.0	95.0	90.0	95.0	93.5	9.5	10.3
40	76.0	86.0	82.0	83.0	81.75	5.75	7.0
35	70.0	76.0	71.0	73.0	72.5	3.5	4.8
30	60.0	68.0	61.0	66.0	63.75	4.25	6.7
25	48.0	54.0	54.0	54.0	52.5	4.5	8.6
20	39.0	49.0	46.0	46.0	45.0	6.0	13.3
15	28.0	36.0	36.0	38.0	34.5	6.5	18.8
10	22.0	25.0	25.0	26.0	24.5	2.5	10.2
5	14.0	15.0	20.0	22.0	17.75	4.25	24.0
0	0.0	5.0	0.0	0.0	1.25	3.75	300.0
Extra Galvanometer - 5,000 p.p.m. Na used as high standard							
5,000	100.0	100.0	103.0	100.0	100.75	2.25	2.2
4,000	78.5	83.0	83.0	82.0	81.62	3.12	3.82
3,000	72.0	75.0	76.0	76.5	74.89	2.87	3.84
2,000	64.0	66.0	64.5	65.0	64.87	1.13	1.74
1,000	51.0	50.5	49.5	49.0	50.0	1.0	2.0
500	29.5	31.25	30.75	30.5	30.5	1.0	3.7
400	27.5	28.0	27.0	26.5	27.25	.75	2.75
300	22.25	23.75	22.5	22.5	22.75	1.0	4.4
200	17.75	18.75	17.25	17.0	17.69	1.06	6.0
100	10.25	11.5	9.75	10.25	10.44	1.06	10.1
90	10.0	10.5	9.25	9.25	9.75	.75	7.7
80	9.0	9.5	8.25	8.75	8.88	.63	7.1
70	8.0	8.75	7.5	7.5	7.94	.81	10.2
60	6.75	7.75	6.25	6.75	6.87	.88	12.8
50	6.0	6.5	5.5	5.75	5.94	.56	9.4
45	5.0	5.75	4.75	5.0	5.12	.63	12.3
40	4.75	5.5	4.25	4.5	4.75	.75	15.8
35	4.25	4.5	3.75	4.0	4.12	.37	9.0
30	4.0	4.25	3.5	3.75	3.87	.38	9.8
25	3.75	3.75	3.0	3.0	3.37	.37	11.0
20	3.0	3.0	2.25	2.5	2.69	.44	16.3
15	2.5	2.5	1.5	1.75	2.06	.56	27.2
10	1.75	1.5	1.0	1.0	1.31	.44	33.6

TABLE III (Continued)

INSTRUMENT READINGS

P.P.M.	1st.	2nd.	3rd.	4th.	Average	Maximum Deviation	Percent Deviation
Extra Galvanometer - 5,000 p.p.m. Na used as high standard (Continued)							
5	1.0	.75	.5	.75	.75	.25	33.3
0	.5	.25	0.0	0.0	.19	.31	163.0
Extra Galvanometer - 500 p.p.m. Na used as high standard							
500	100.0	100.0	105.0	105.0	102.5	2.5	2.44
400	86.0	89.0	88.0	88.0	87.75	1.75	1.99
300	71.0	76.75	76.0	73.5	74.31	3.31	4.45
200	55.0	59.5	59.0	57.25	57.69	2.69	4.66
100	35.0	37.75	35.0	33.75	35.37	2.38	6.73
90	32.25	34.25	31.25	31.0	32.18	2.07	6.43
80	29.25	31.5	28.5	28.0	29.31	2.19	7.47
70	26.25	28.25	26.5	25.5	26.62	1.63	6.12
60	22.75	25.0	23.25	22.0	23.25	1.75	7.53
50	19.5	21.5	19.0	18.75	19.68	1.82	9.25
45	18.75	19.0	17.5	17.0	18.06	1.06	5.87
40	16.0	17.75	15.5	15.5	16.18	1.57	9.70
35	15.25	16.0	14.0	14.0	14.81	1.19	8.04
30	13.0	14.25	11.75	12.75	12.93	1.32	10.21
25	10.75	12.5	10.5	10.5	11.06	1.44	13.02
20	9.5	10.0	8.75	9.0	9.31	.69	7.41
15	7.25	8.0	6.75	7.5	7.37	.63	8.55
10	5.25	6.0	4.75	5.25	5.31	.69	13.0
5	3.75	4.75	3.5	3.75	3.93	.83	21.12
0	.5	.75	.0	.0	.31	.44	141.94
Extra Galvanometer - 50 p.p.m. Na used as high standard							
50	100.0	100.0	102.0	103.0	101.25	1.75	1.73
45	92.25	92.75	91.0	91.0	91.75	1.0	1.09
40	84.0	80.5	82.0	82.0	82.13	1.87	2.28
35	74.0	74.75	75.0	73.5	74.31	.81	1.09
30	65.5	63.75	62.5	62.0	63.44	2.06	3.25
25	57.0	55.5	52.5	53.5	54.63	2.37	4.38
20	47.5	45.5	44.5	44.0	45.38	2.12	4.67
15	37.0	35.5	34.0	33.75	35.06	1.94	5.53
10	26.75	25.0	24.5	24.5	25.19	1.56	6.19
5	16.5	15.0	14.5	14.0	15.0	1.50	10.0
0	5.75	1.0	.0	.0	1.69	4.06	240.24
Built-in Galvanometer - 5,000 p.p.m. K used as high standard							
5,000	100.0	100.0	98.0	105.0	100.75	4.25	4.22
4,000	79.0	81.0	78.0	87.0	81.25	5.75	7.08

TABLE III (Continued)

INSTRUMENT READINGS

P.P.M.	1st.	2nd.	3rd.	4th.	Average	Maximum Deviation	Percent Deviation
Built-in Galvanometer - 5,000 p.p.m. K used as high standard (Continued)							
3,000	79.0	79.0	74.0	87.0	79.75	7.25	9.09
2,000	64.0	63.0	61.0	69.0	64.25	4.75	7.39
1,000	43.0	44.0	42.0	49.0	44.5	4.5	10.11
500	27.0	29.0	26.0	30.0	28.0	2.0	7.14
400	21.0	24.0	21.0	24.0	22.5	1.5	6.67
300	19.0	21.0	18.0	21.0	19.75	1.75	8.86
200	14.5	16.0	13.5	16.0	15.0	1.5	10.0
100	8.0	9.0	6.25	8.0	7.81	1.56	19.97
90	7.0	8.0	6.0	7.25	7.06	1.06	15.01
80	6.0	7.25	5.25	6.25	6.19	1.06	17.12
70	5.5	6.5	4.75	5.75	5.63	.87	15.45
60	4.5	5.75	4.0	5.0	4.81	.94	19.54
50	3.75	5.0	3.25	4.0	4.0	1.0	25.0
45	3.5	4.0	3.0	3.75	3.56	.56	15.73
40	3.25	3.75	2.5	3.25	3.19	.69	21.63
35	3.0	3.25	1.75	2.75	2.69	.94	34.94
30	2.75	3.0	1.5	2.25	2.38	.88	36.97
25	2.0	2.25	1.25	1.75	1.81	.56	30.94
20	1.5	1.75	1.0	1.25	1.38	.38	27.54
15	1.0	1.25	.75	1.0	1.0	.25	25.0
10	.5	.75	.5	1.0	.69	.31	44.93
5	.5	.5	.5	1.0	.63	.27	42.86
0	.5	.25	0.0	0.0	.19	.31	163.16
Built-in Galvanometer - 500 p.p.m. K used as high standard							
500	100.0	100.0	99.0	104.0	100.75	3.25	3.26
400	75.0	80.0	74.0	81.0	77.5	3.5	4.52
300	69.5	70.0	66.0	71.0	69.13	3.13	4.53
200	50.0	53.0	48.0	53.0	51.0	3.0	5.88
100	29.0	31.0	26.5	27.0	28.38	2.62	9.23
90	26.5	27.0	23.5	24.0	25.25	1.75	6.93
80	23.5	24.0	21.0	22.0	22.63	1.63	7.20
70	20.5	22.0	18.5	18.0	19.75	2.25	11.39
60	19.0	19.0	14.5	15.0	16.88	2.38	14.10
50	15.0	16.0	12.5	12.75	14.06	1.94	13.8
45	13.0	14.75	11.0	11.25	12.5	2.25	18.0
40	12.25	12.75	9.75	10.25	11.25	1.5	13.33
35	10.5	12.25	8.0	8.5	9.81	2.44	24.87
30	9.5	9.75	7.25	8.0	8.63	1.38	15.99
25	8.0	8.25	5.75	5.75	6.94	1.31	18.88
20	6.0	7.0	4.5	4.25	5.44	1.56	28.68
15	4.5	5.25	3.5	3.25	4.13	1.12	27.12
10	3.5	3.5	3.0	2.25	3.06	.81	26.47

TABLE III (Continued)

INSTRUMENT READINGS

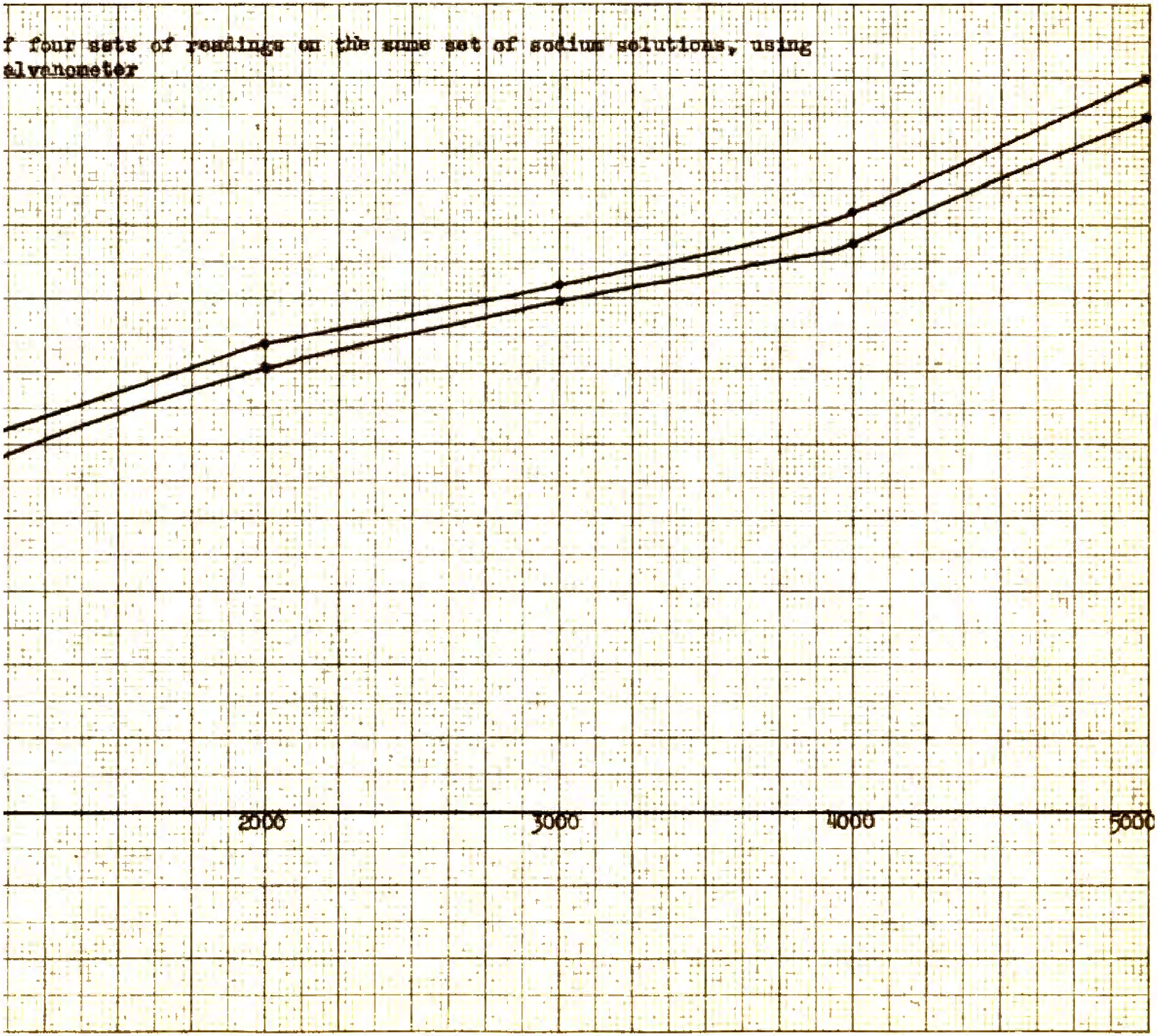
P.P.M.	1st.	2nd.	3rd.	4th.	Average	Maximum Deviation	Percent Deviation
Built-in Galvanometer - 500 p.p.m. K used as high standard (Continued)							
5	1.5	1.5	.75	2.25	1.5	.75	50.0
0	.75	.5	.0	.0	.31	.44	141.94
Built-in Galvanometer - 50 p.p.m. K used as high standard							
50	100.0	100.0	99.0	103.0	100.5	2.5	2.49
45	88.0	94.0	87.0	92.0	90.25	3.75	4.16
40	78.0	88.0	79.0	83.0	82.0	6.0	7.32
35	72.0	73.0	67.0	71.0	70.75	3.75	5.30
30	65.0	63.0	58.0	61.0	61.75	3.75	6.07
25	52.0	51.0	48.0	50.0	50.25	2.25	4.48
20	42.0	38.0	38.0	38.0	39.0	3.0	7.69
15	33.0	28.0	28.5	28.0	29.38	3.62	12.32
10	25.0	22.0	20.5	18.0	21.38	3.62	16.93
5	17.0	9.0	13.5	10.0	12.38	4.62	37.32
0	10.0	0.0	0.0	0.0	2.5	7.5	300.0
Extra Galvanometer - 5,000 p.p.m. K used as high standard							
5,000	100.0	100.0	105.0	99.0	101.0	4.0	3.96
4,000	82.0	76.0	89.0	77.0	81.0	8.0	9.88
3,000	78.0	74.0	85.0	75.0	78.0	7.0	8.97
2,000	63.0	58.0	69.0	59.0	62.25	6.75	10.84
1,000	42.0	42.0	46.0	40.0	42.5	3.5	8.26
500	26.5	27.5	30.0	26.0	27.5	2.5	9.09
400	20.5	21.5	23.0	21.0	21.5	1.5	6.98
300	18.0	19.0	19.0	18.5	18.63	.63	3.38
200	13.5	13.5	13.0	13.25	13.31	.31	2.33
100	7.5	7.5	7.5	7.5	7.5	0.0	0.0
90	6.25	7.0	6.75	6.75	6.69	.44	6.77
80	5.75	6.25	5.75	6.0	5.94	.31	5.22
70	5.0	5.5	5.0	5.0	5.13	.37	7.21
60	4.25	4.5	4.25	4.25	4.31	.19	4.41
50	3.6	4.0	3.75	3.75	3.78	.22	5.82
45	3.25	3.75	3.25	3.25	3.38	.37	10.95
40	3.0	3.25	2.75	3.0	3.0	.25	8.33
35	2.75	3.0	2.25	2.25	2.56	.44	17.19
30	2.25	2.75	1.75	1.75	2.13	.62	29.11
25	1.75	2.0	1.5	1.25	1.63	.38	23.31
20	1.25	1.5	1.0	1.0	1.19	.31	26.05
15	.75	1.0	.75	.75	.81	.19	23.46
10	.5	.75	.5	.5	.56	.19	33.93
5	.3	.5	.5	.5	.45	.15	33.33
0	.2	.25	0.0	0.0	.11	.14	127.27

TABLE III (Continued)

INSTRUMENT READINGS

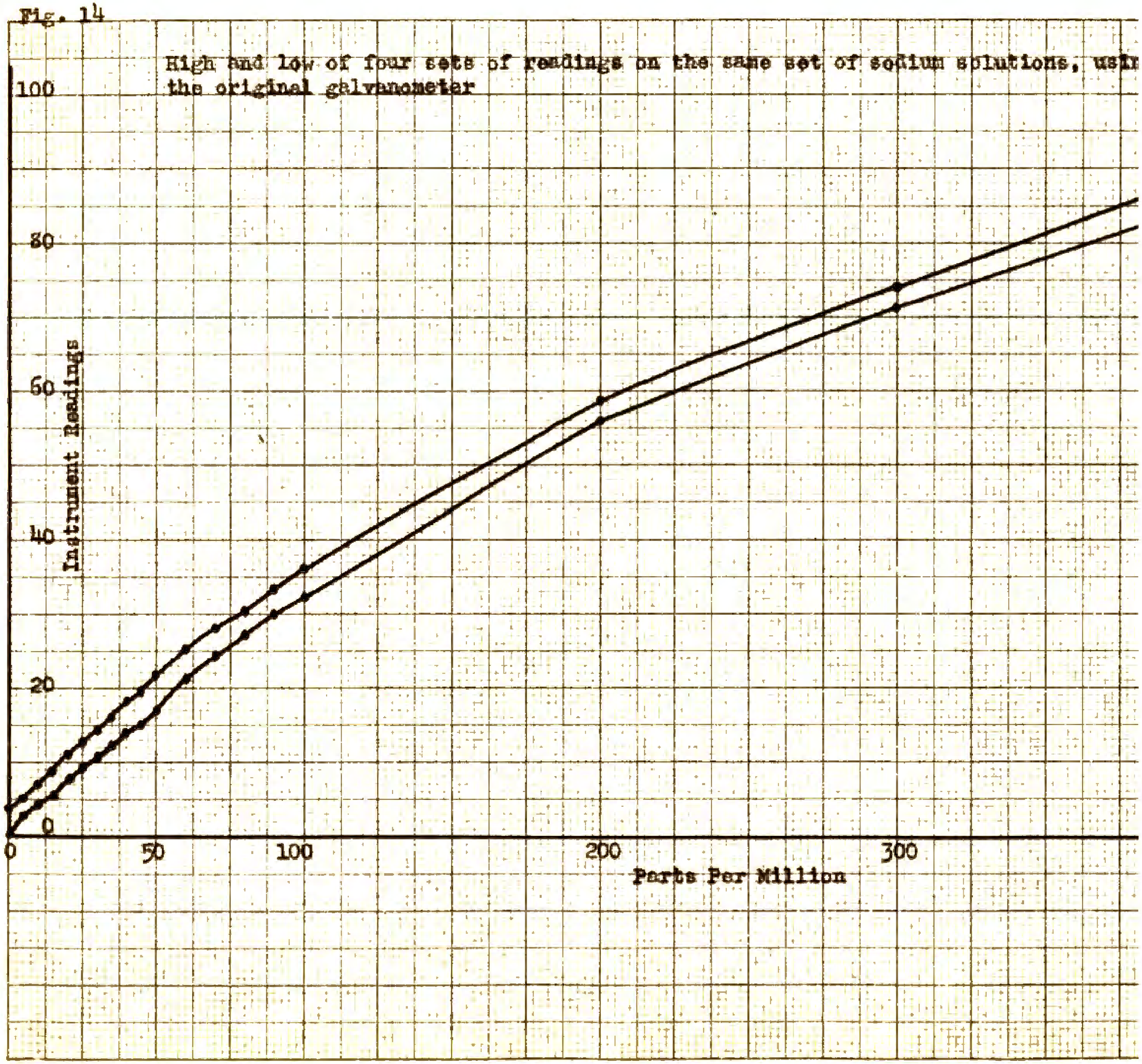
P.P.M.	**1st.**	**2nd.**	**3rd.**	**4th.**	**Average**	**Maximum Deviation**	**Percent Deviation**
Extra Galvanometer - 500 p.p.m. K used as high standard							
500	100.0	100.0	99.0	98.0	99.25	1.25	1.26
400	79.0	80.5	74.5	77.0	77.75	3.25	4.18
300	69.5	75.0	67.0	69.0	69.63	5.37	7.71
200	51.0	54.0	50.0	50.0	51.25	2.75	5.37
100	29.25	30.0	28.0	28.0	28.81	1.19	4.13
90	26.0	27.0	23.0	24.5	25.13	2.13	8.48
80	23.5	24.0	21.75	22.5	22.94	1.19	5.19
70	21.25	22.0	18.75	20.0	20.5	1.75	8.34
60	18.25	17.75	16.0	17.0	17.25	1.25	7.25
50	15.0	14.75	13.25	13.75	14.19	.94	6.62
45	14.0	13.5	12.0	13.25	13.19	1.19	9.02
40	12.75	12.0	10.75	12.0	11.88	1.13	9.51
35	11.5	10.75	9.25	10.0	10.38	1.13	10.89
30	10.25	9.25	8.25	8.5	9.06	1.19	13.13
25	8.5	8.0	6.5	7.25	7.56	.94	12.43
20	7.0	6.25	4.75	5.75	5.94	1.19	20.03
15	5.5	4.0	3.75	4.0	4.31	1.19	27.61
10	4.0	3.0	2.75	3.0	3.19	.81	25.39
5	2.75	1.0	1.5	1.75	1.75	1.0	57.14
0	1.25	.25	0.0	0.0	.38	.87	225.95
Extra Galvanometer - 50 p.p.m. K used as high standard							
50	100.0	100.0	103.0	99.0	100.5	2.5	2.49
45	89.0	86.5	91.0	87.5	88.5	2.5	2.82
40	82.75	81.0	79.75	79.75	80.81	1.94	2.40
35	73.0	75.5	69.5	69.5	71.88	3.62	5.05
30	61.75	63.0	60.0	59.5	61.06	1.94	3.18
25	51.25	53.0	49.5	49.25	50.75	2.25	4.43
20	41.25	42.0	40.75	40.5	41.13	.87	2.12
15	31.0	31.25	30.0	30.5	30.69	.69	2.25
10	20.5	20.0	19.75	19.75	20.0	.5	2.5
5	10.5	8.25	10.75	10.0	9.88	1.63	16.5
0	1.25	-1.0	0.0	0.0	.06	1.19	1,980.0

The essential information from these last tables is presented graphically in Fig's. 13 - 24. The distance between the two curves in any figure, if measured vertically represents the variation of instrument reading at that particular concentration; if measured horizontally represents the variation of concentrations to be expected from that given instrument reading.



f four sets of readings on the same set of sodium solutions, using
alvanometer

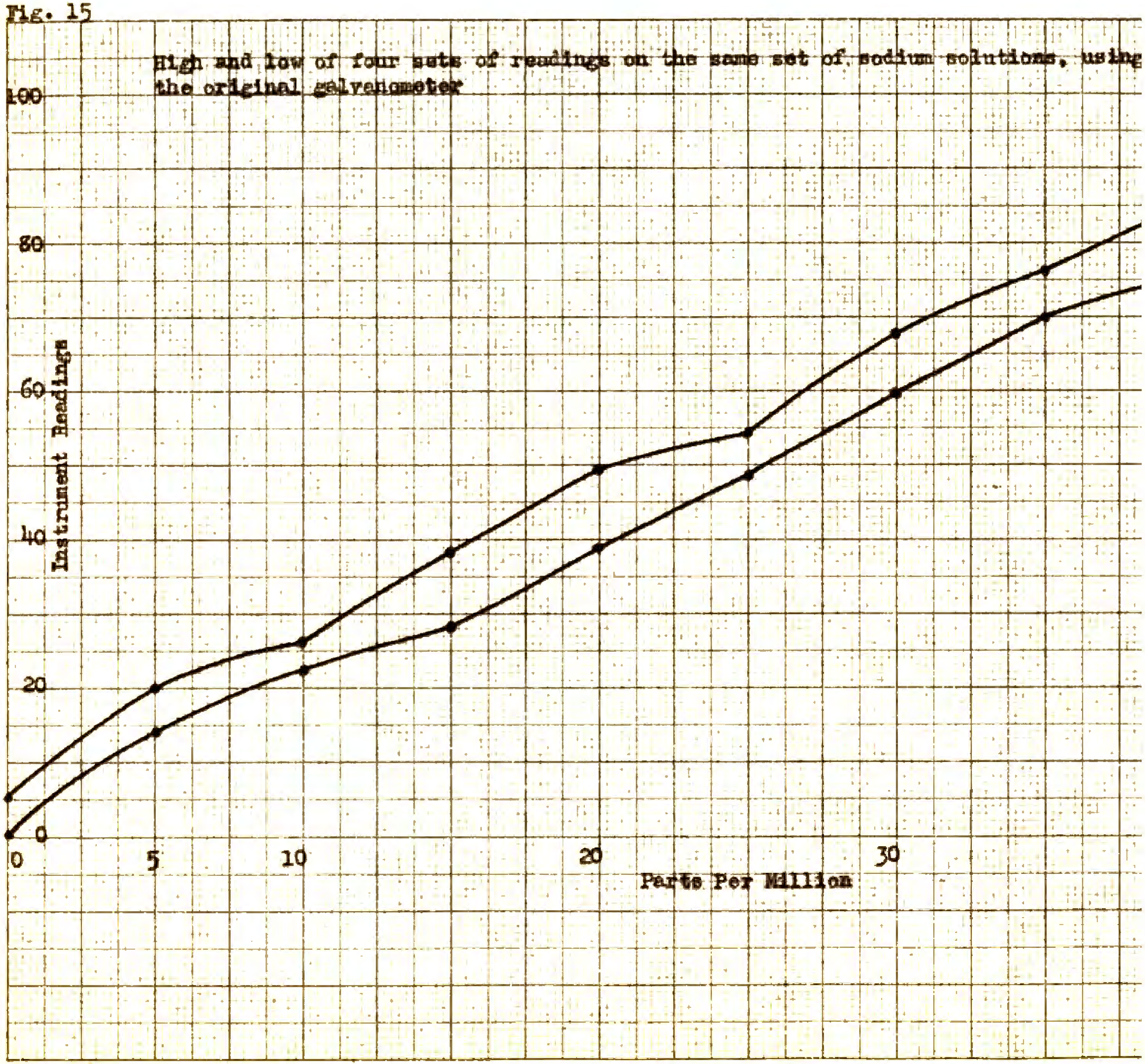
Fig. 14



High and low of four sets of readings on the same set of sodium solutions, usin
the original galvanometer

Fig. 14

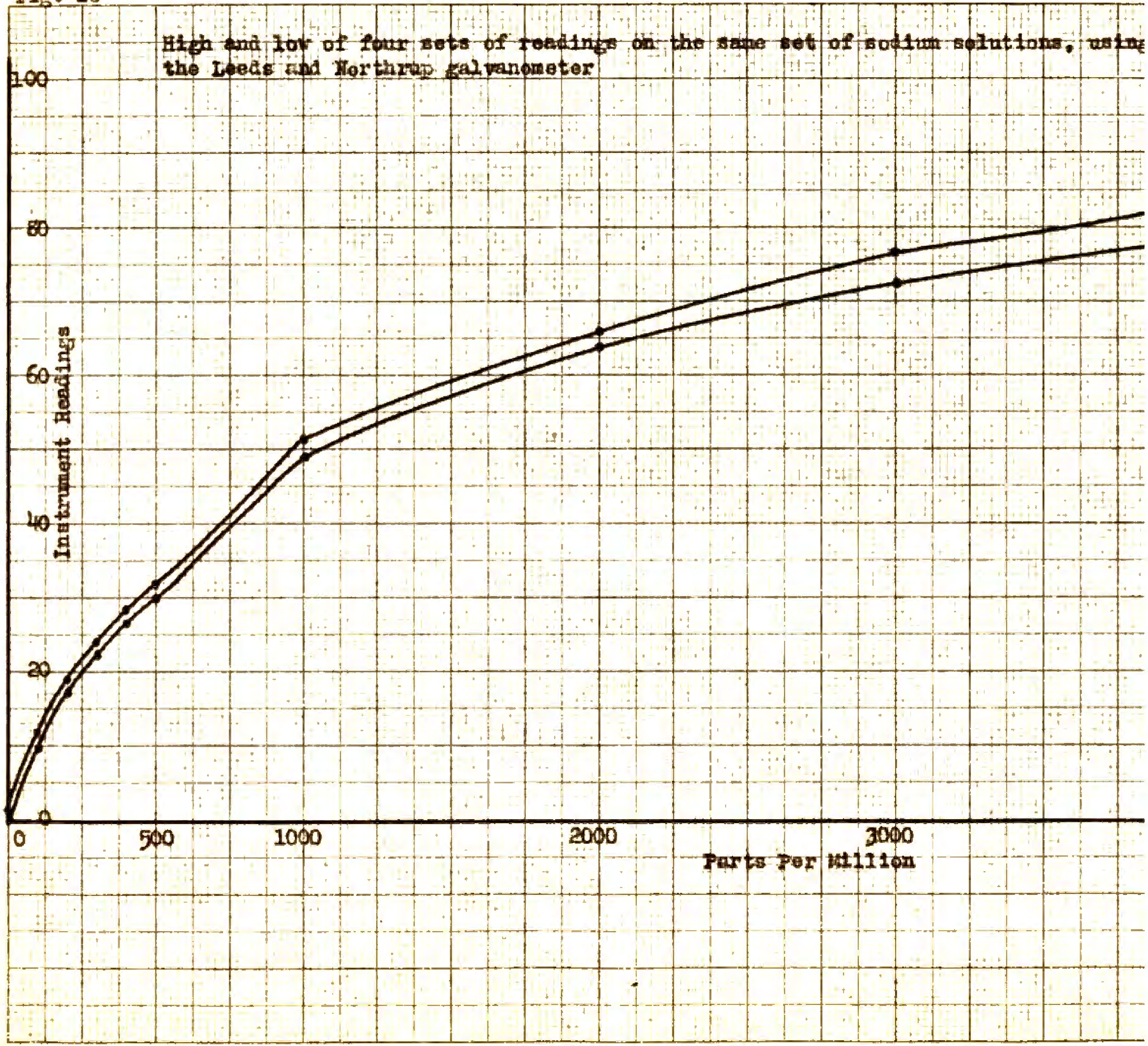
Fig. 15



High and low of four sets of readings on the same set of sodium solutions, using the original galvanometer

Fig. 15

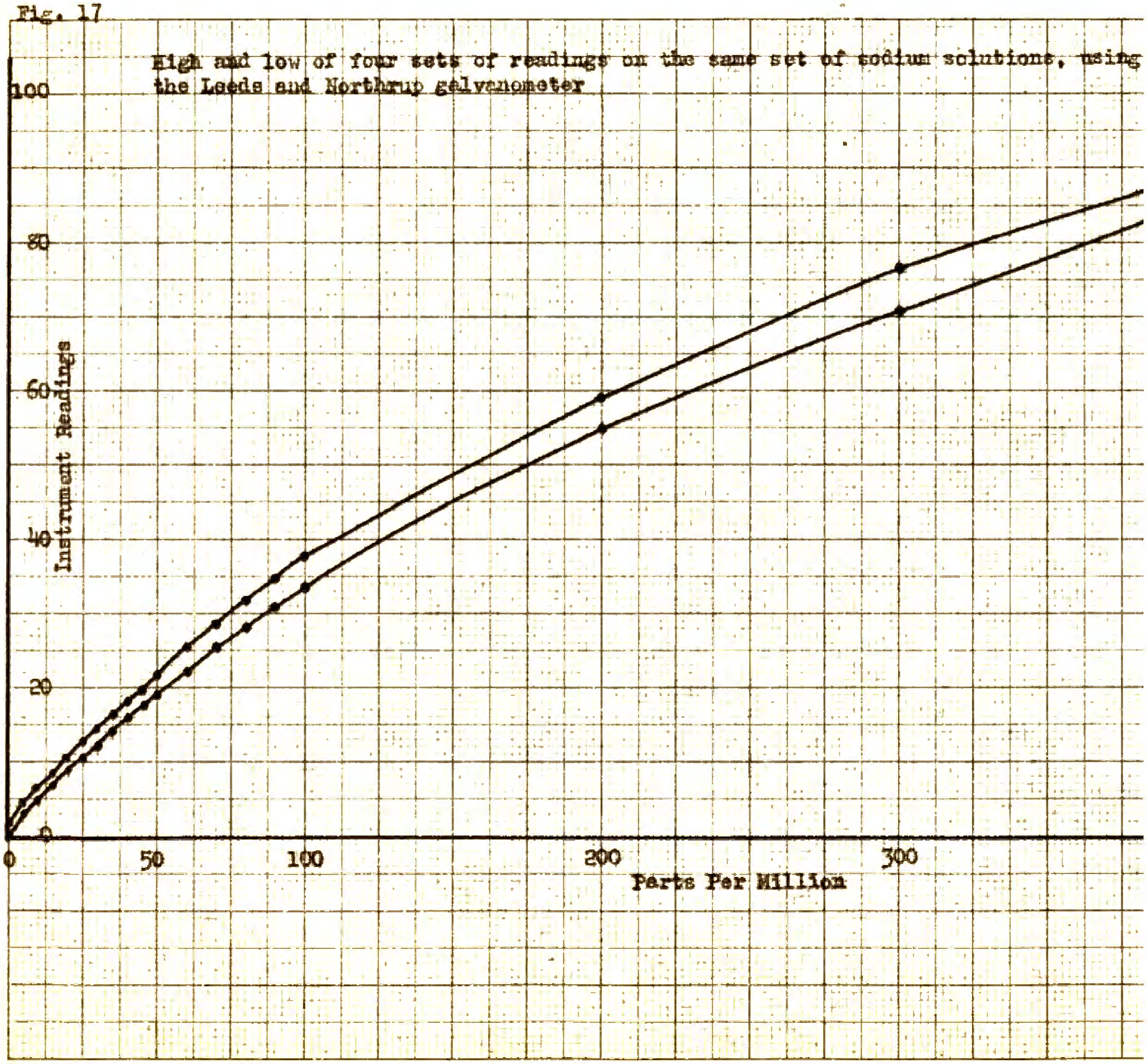
Fig. 16



High and low of four sets of readings on the same set of sodium solutions, using the Leeds and Northrup galvanometer

Fig. 16

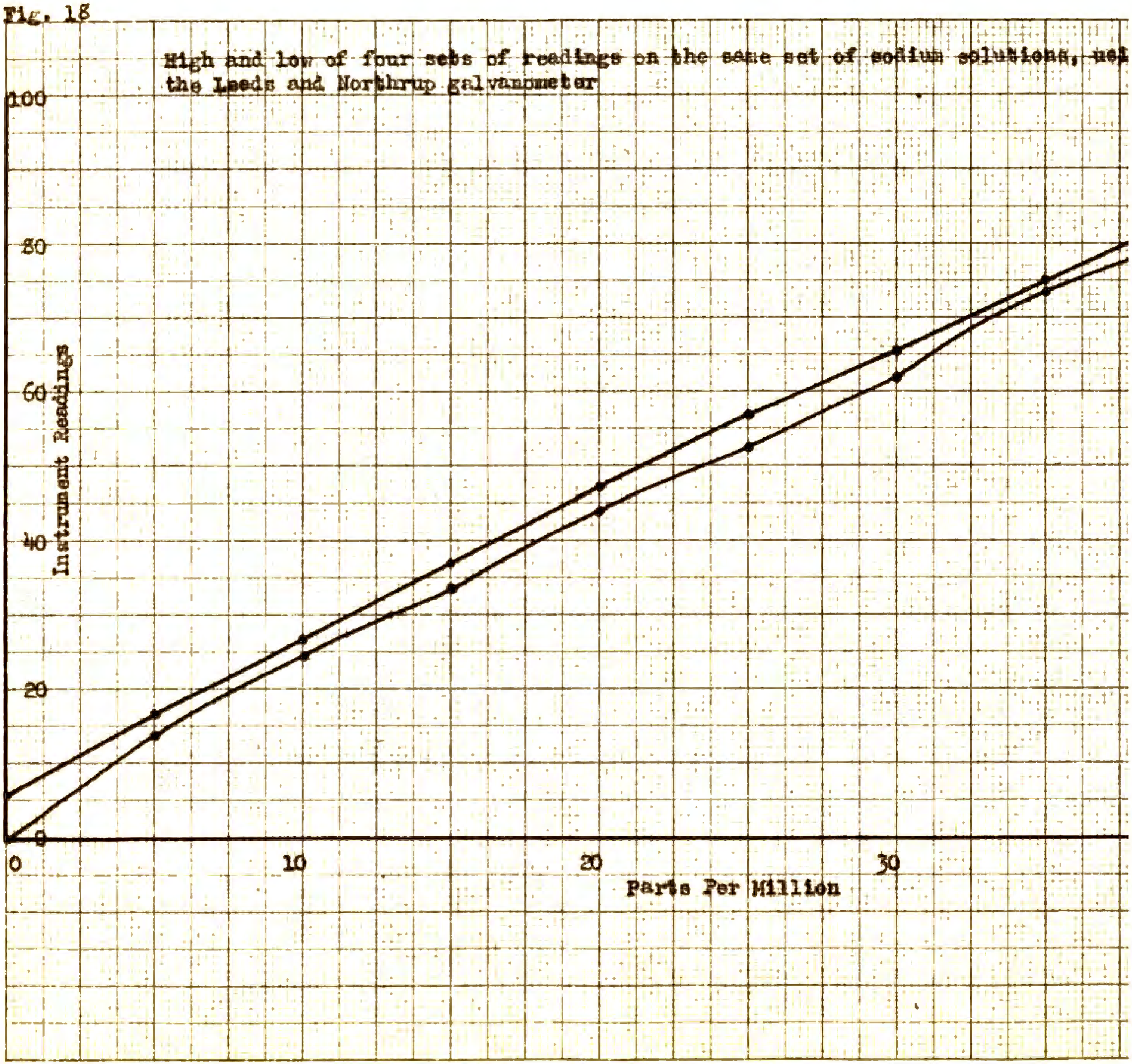
Fig. 17



High and low of four sets of readings on the same set of sodium solutions, using the Leeds and Northrup galvanometer

Fig. 17

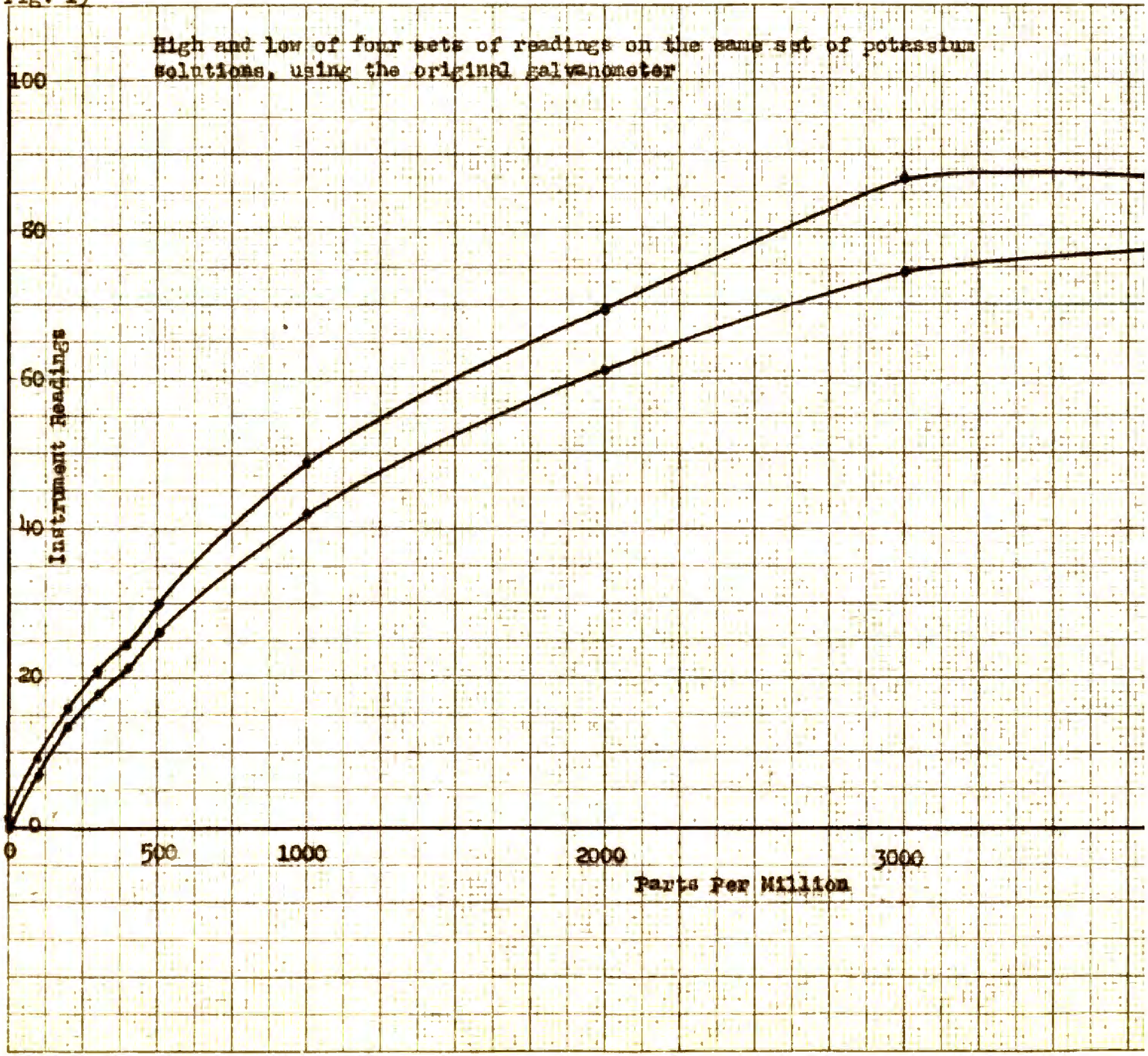
Fig. 18



High and low of four sets of readings on the same set of sodium solutions, usi
the Leeds and Northrup galvanometer

Fig. 18

Fig. 19



High and low of four sets of readings on the same set of potassium solutions, using the original galvanometer

Fig. 19

Fig. 20

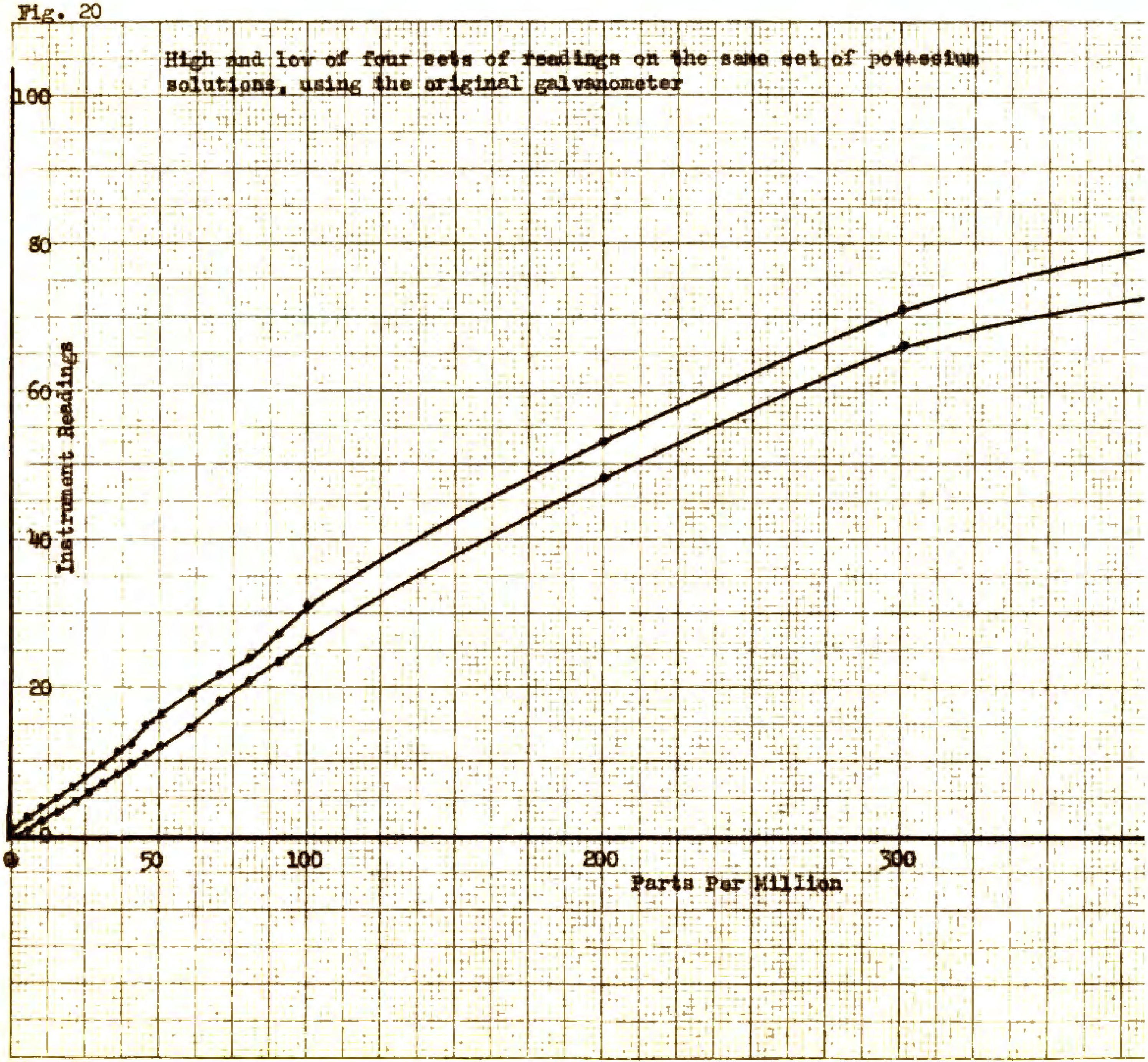
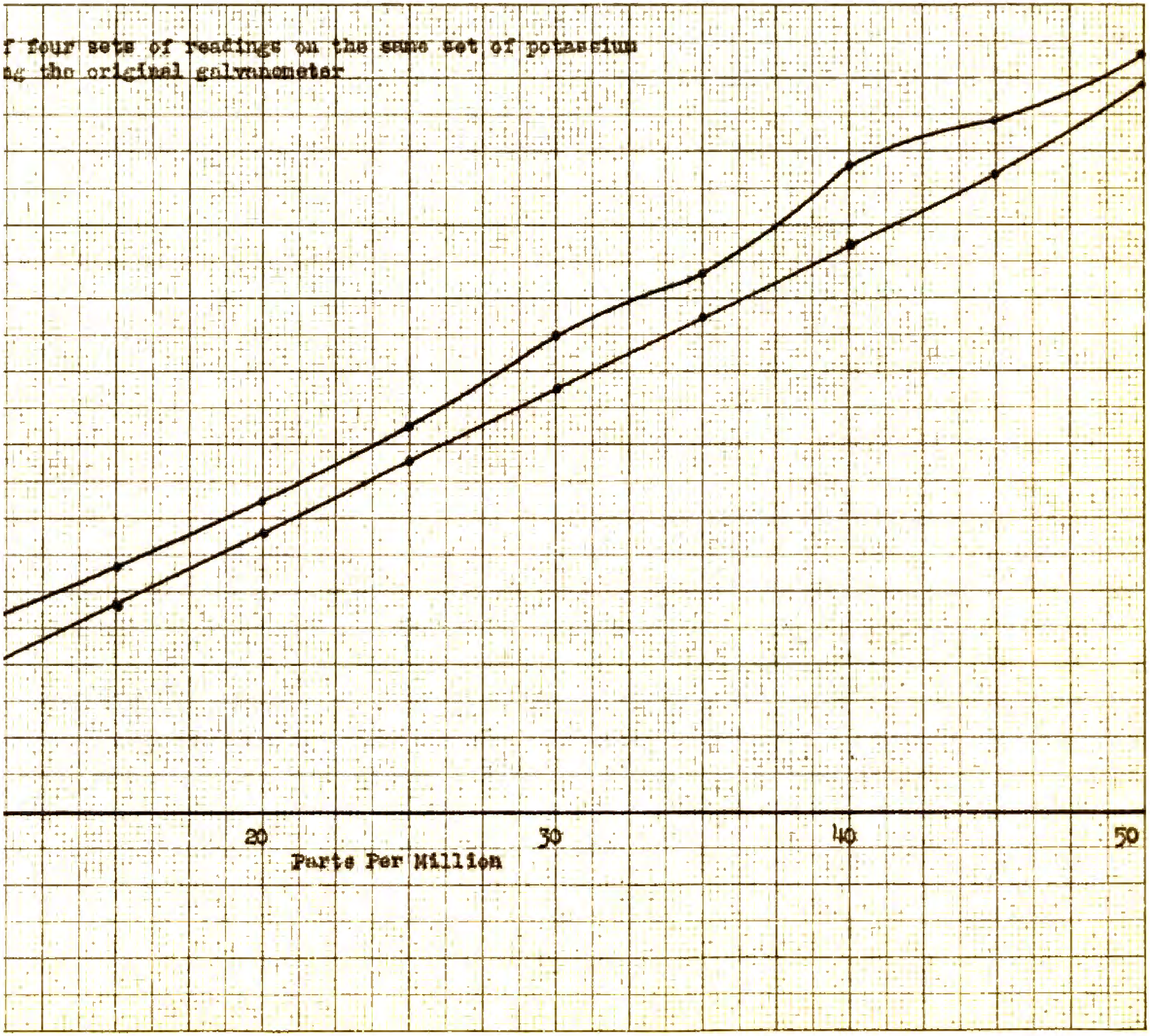
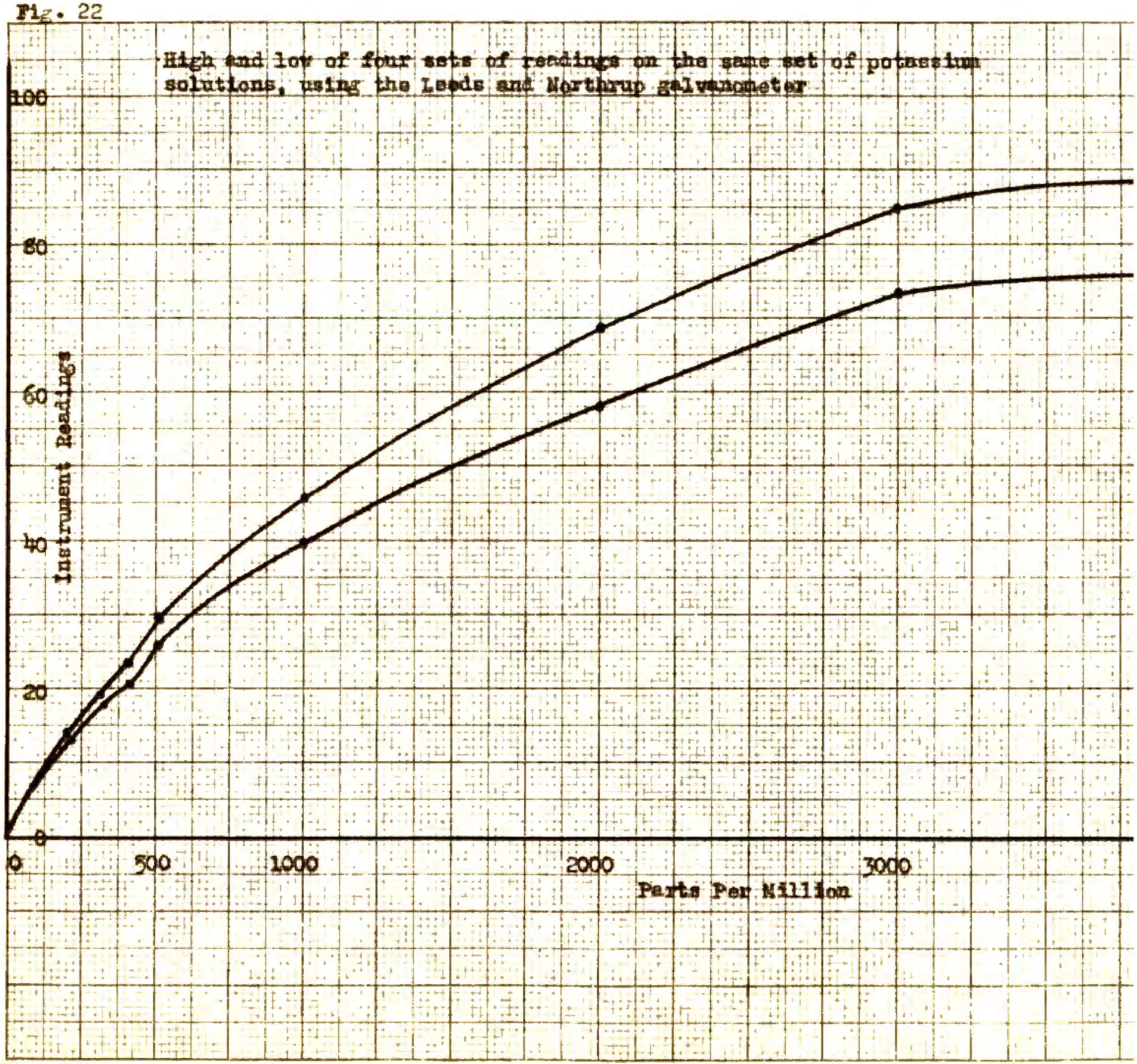

High and low of four sets of readings on the same set of potassium solutions, using the original galvanometer
100
80
60
40
20
0
Instrument Readings
0
50
100
200
300
Parts Per Million

Fig. 20



f four sets of readings on the same set of potassium
ng the original galvanometer

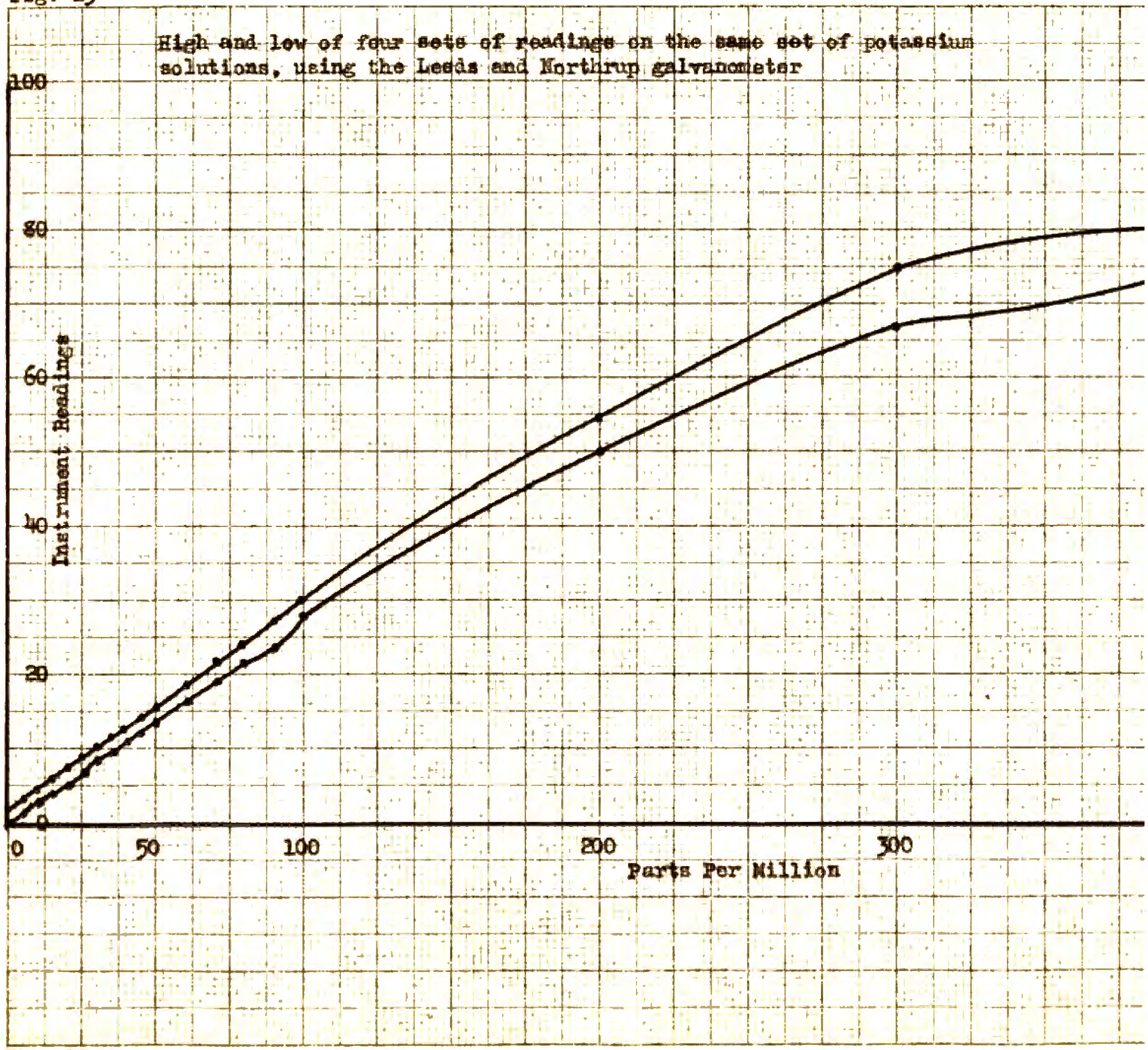
Fig. 22



High and low of four sets of readings on the same set of potassium solutions, using the Leeds and Northrup galvanometer

Fig. 22

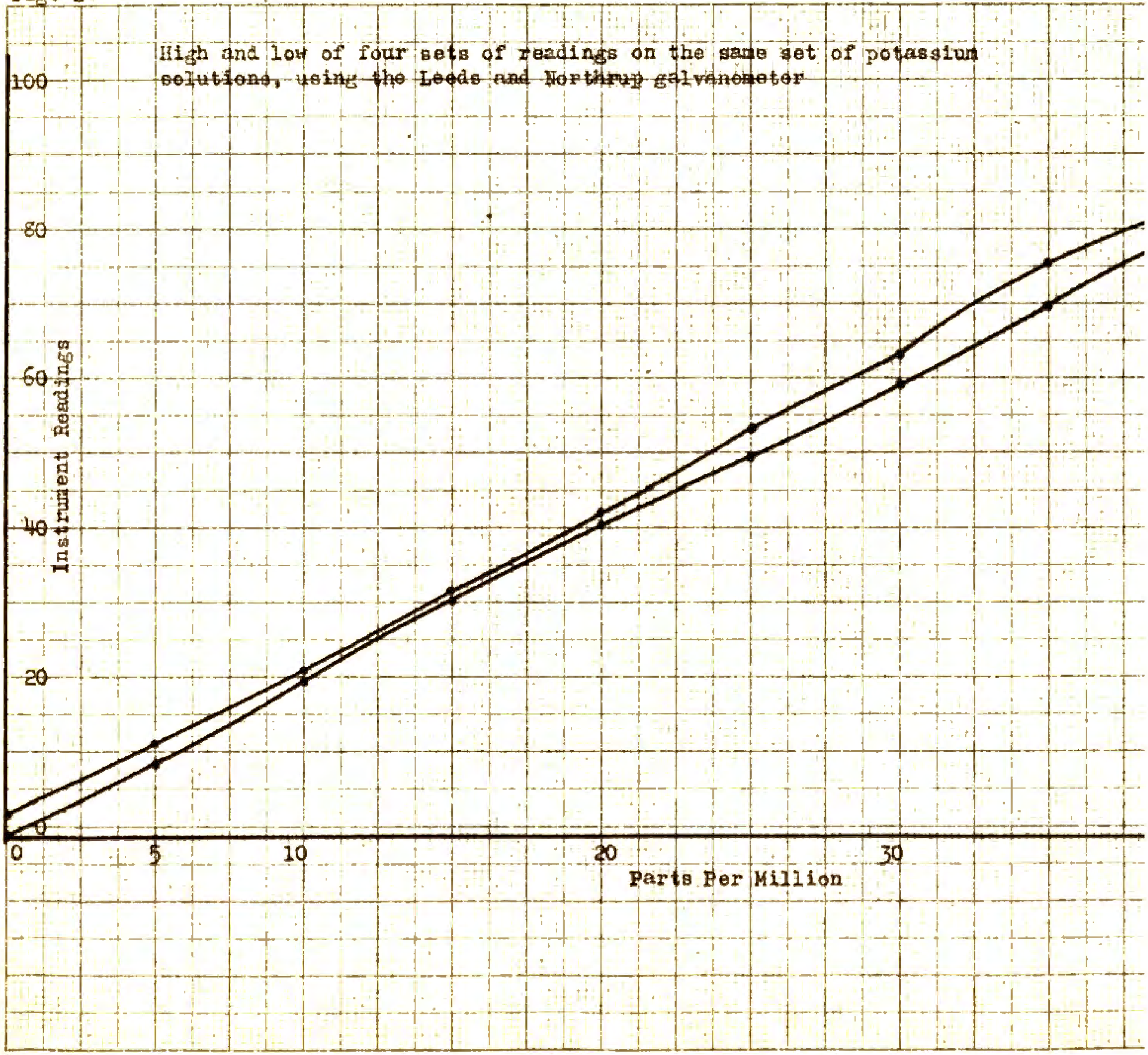
Fig. 23



High and low of four sets of readings on the same set of potassium solutions, using the Leeds and Northrup galvanometer

Fig. 23

Fig. 24



High and low of four sets of readings on the same set of potassium solutions, using the Leeds and Northrup galvanometer

Fig. 24

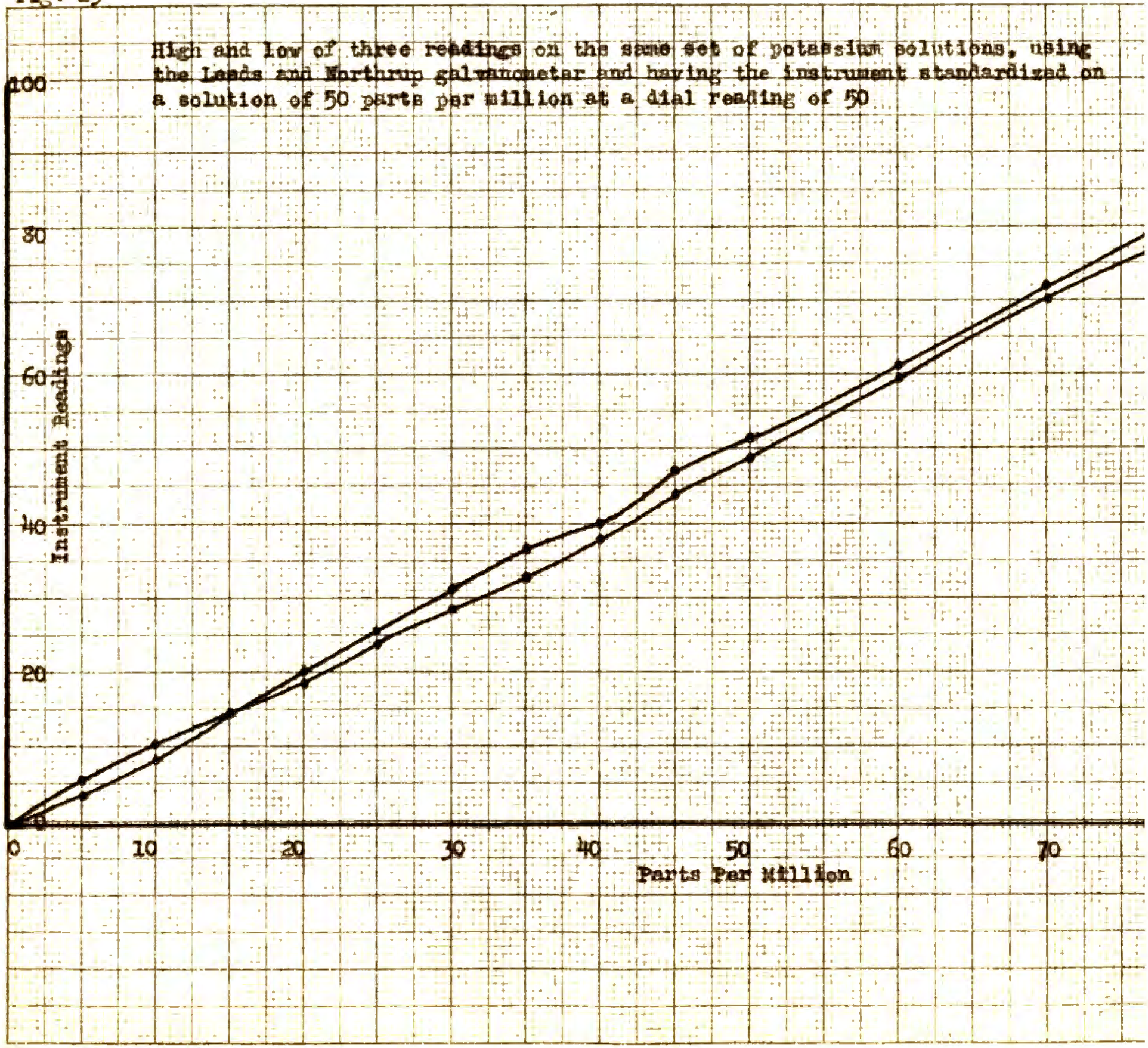
Most of these graphs show a reversal in change of slope somewhere near the instrument reading of 80. When these observations were first plotted it was feared that some error in preparing solutions caused this reversal of slope; therefore, new solutions were made and used to determine points at closer intervals between instrument readings of 70 and 90. The readings thus obtained completely confirmed the shape of the original curves.

As has been previously mentioned in this report, the instrument seems to be more accurate at relatively low concentrations. Also, it is to be noted from Fig's. 13 - 24 that the standard curves seem to have irregular deviation between instrument readings of 80 and 90. To eliminate the error due to standardizing the instrument at a point above this irregular portion of the curve, a set of readings was taken on standard solutions with the zero point on the dial standardized against distilled water as usual but with a high standard of 50 parts per million standardised at a reading of 50 on the instrument dial. Fig's. 25 - 26 show the results of these observations. To furnish a basis of comparison for these two sets of readings, another set of observations was made in which the instrument was standardized on 100 part per million standards with the instrument dial set at 100. The result of these observations is shown in Fig's. 27 - 28. From these observations it appears that slightly more consistent results may be obtained by standardizing the instrument at a dial reading below the above mentioned irregularities.

In view of the results shown in Fig's. 13 - 28, it would seem that the most accurate analyses can be made by following this procedure:

1. Run the original sample on the instrument using standard solution of sufficient concentration to insure that the reading will fall on the graduated part of the dial.

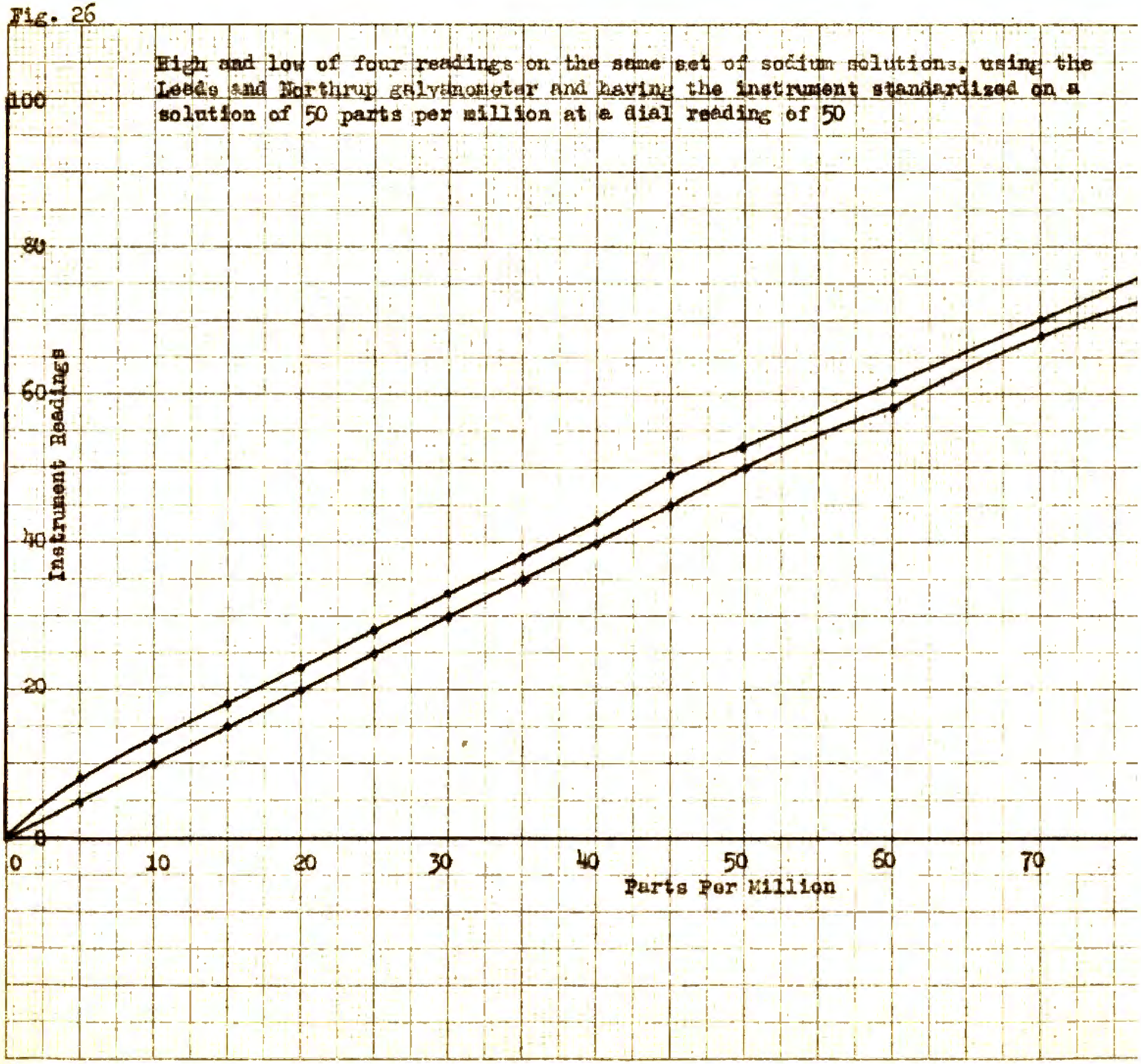
Fig. 25



High and low of three readings on the same set of potassium solutions, using the Leeds and Northrup galvanometer and having the instrument standardized on a solution of 50 parts per million at a dial reading of 50

Fig. 25

Fig. 26



High and low of four readings on the same set of sodium solutions, using the Leeds and Northrup galvanometer and having the instrument standardized on a solution of 50 parts per million at a dial reading of 50

Fig. 26

Fig. 27

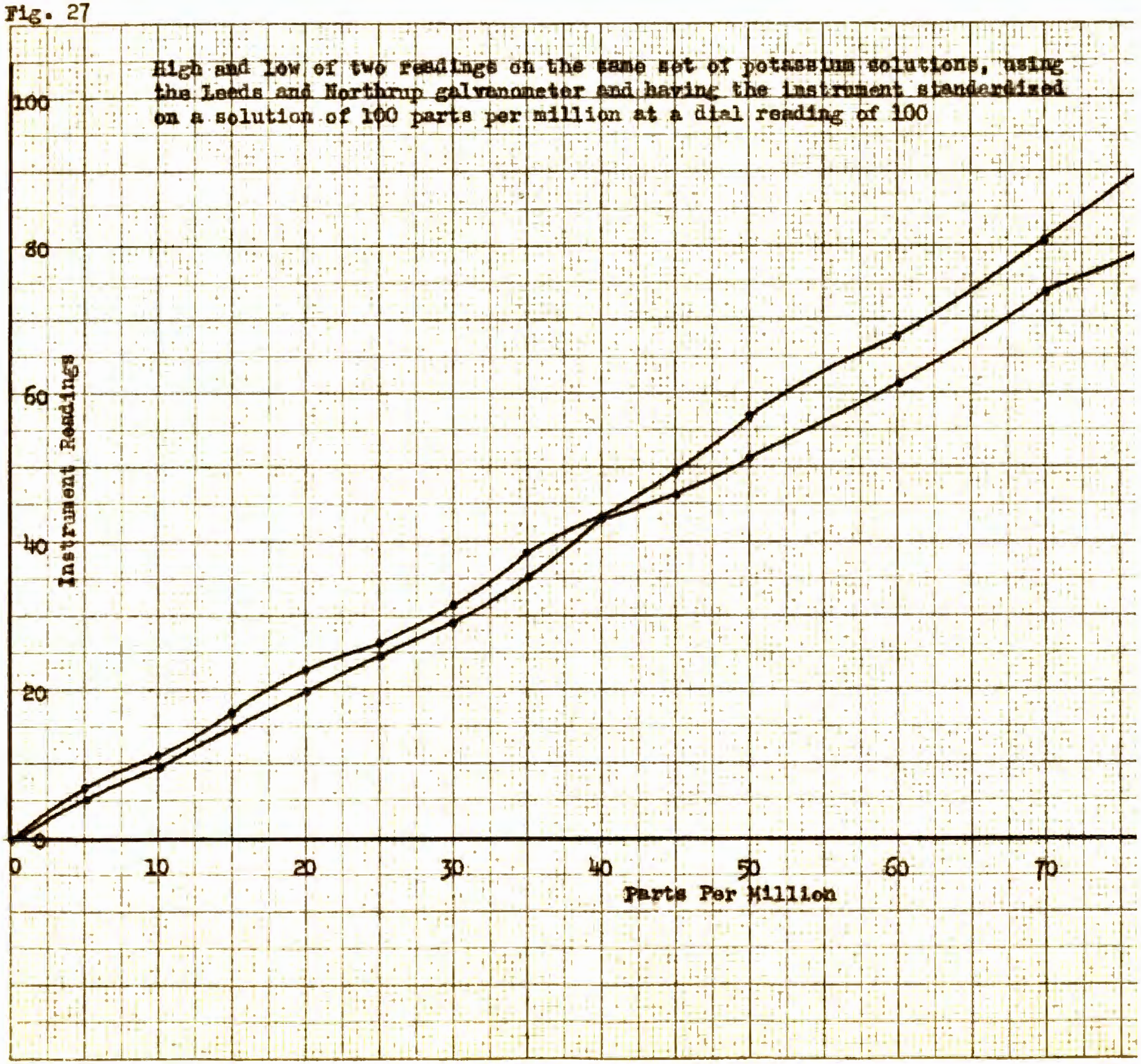
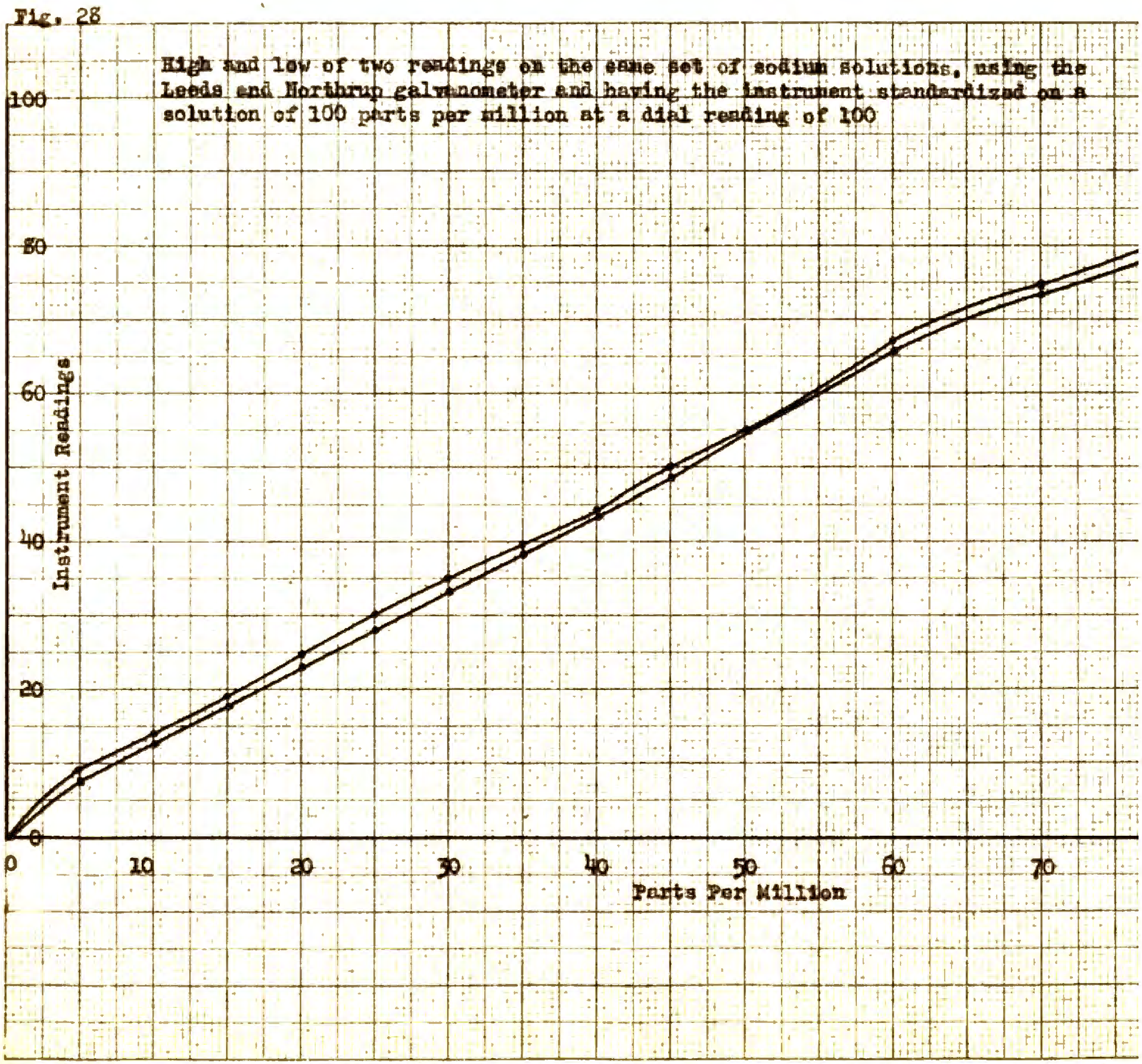

High and low of two readings on the same set of potassium solutions, using the Leeds and Northrup galvanometer and having the instrument standardized on a solution of 100 parts per million at a dial reading of 100

Fig. 27

Fig. 28



High and low of two readings on the same set of sodium solutions, using the Leeds and Northrup galvanometer and having the instrument standardized on a solution of 100 parts per million at a dial reading of 100

Fig. 28

2. Run the analyses with the instrument standardized at the mid-point of the dial on a standard solution of 50 parts per million. (If necessary dilute the samples to a known fraction of their original concentration so that the reading will fall between 10 and 80 on the graduated dial when set against such standard.)
3. In order to gain benefits from using such a low concentrated solution for standard, it would seem to be necessary to use a more accurate galvanometer than the one originally furnished with the instrument.

It seems probable that even more accuracy might be had by using standard solutions with concentrations less than 50 parts per million, if the more accurate galvanometer were used. Observations were not run to prove this point, but it is certain that the original galvanometer could not be profitably used in this extremely low concentration range.

COMPARISON WITH ANALYSES BY OTHER METHODS

A set of 18 prepared brine samples was submitted by the Stanolind Oil Company to be analyzed on the flame photometer. The potassium content of these samples ranged from 125 to 9,890 parts per million, the sodium content from 37,000 to 74,000 parts per million, the calcium content from 880 to 8,885 parts per million, and the magnesium content from 650 to 1,325 parts per million. No effort was made to remove the calcium or magnesium before analysis for sodium and potassium. Most of these samples had to be diluted to a known percent of their original concentration to get them in a range less than 500 p.p.m. before they could be run on the flame photometer. Comparison of the analysis by the flame photometer and the analysis run by the Stanolind Oil Company Laboratory gives the following figures: On potassium a maximum difference of 2,260 parts per million or a maximum percentage difference of 42, and a minimum difference of 6 parts per million, or a minimum percentage difference of 1.8 and an average percentage difference of 20.1; on sodium a maximum difference of 28,427 parts per million or a maximum percentage difference of 75.9, and a minimum difference of 37 parts per million, or a minimum percentage difference of 0.1 and an average percentage difference of 28.4.

All the other comparisons were made using samples of natural surface or ground waters which had been previously analyzed by the Water Resources Division of the U. S. Geological Survey. The first group of these consisted of 34 samples. The highest content of potassium in this group was 14 parts per million and all the rest were below 6 parts per million. The average difference in the two analyses was 2.07 parts per million, or an average percentage difference of 33.6. The maximum sodium content of any sample was 600 parts per million. Of the samples having less than 25 parts per million, the average difference between the two analyses was 3.36 parts per million, or 21.3%. Of the samples having above 25 parts per million, the average percentage difference between the two methods was 12.33.

A new step was introduced into the procedure in analyzing the next group of 44 samples. This step consisted in making both standards and sample solutions approximately .01 N with HCl. The highest potassium content of any sample in this group was 14 parts per million, and in 33 samples it was less than 5 parts per million. The average difference between the two sets of analyses was 1.2 parts per million, or an average percentage difference of 25.3. The highest sodium content of any sample in this group was 1,675 parts per million. On the 24 samples of this group which had below 25 parts per million sodium, the average difference between the two sets of analyses was 1.96 parts per million, or an average percentage difference of 20.2. On the other 20 samples of this group in which the sodium content was above 25 parts per million, the average percentage difference between the two sets of analyses was 7.7.

The third group of samples was run without the treatment of HCl but using the more sensitive Leeds and Northrup galvanometer. Of the 21 samples in this group, the highest concentration of potassium found was 11 parts per million. The average difference between the two sets of analyses for potassium was 2.29 parts per million, or an average percentage difference of 44.0. Fifteen of the samples in this group had less than 25 parts per million of sodium. The average difference between the analyses of these was 2.15 parts per million, or an average percentage difference of 21.7. Five of the samples in this group had over 25 parts per million sodium, and the average percentage difference between the two analyses for these was 14.9.

A fourth set of samples was analyzed using the Leeds and Northrup galvanometer and following the procedure suggested on Pages 26 and 27 (not using the HCl treatment). This set consisted of 12 samples. The highest concentration of potassium in any sample was 5.1 parts per million, and the average difference between the two analyses was 1.71 parts per million, or an average percentage difference of 59.6. The average percentage difference between the two analyses for sodium on the four samples which contained over 25 parts per million was 22.2. The average difference between the two analyses for sodium on the 8 samples which contained less than 25 parts per million was 8.4 parts per million, or an average percentage difference of 63.2.

From the results thus obtained on the check analyses of ground and surface waters, it would seem that the addition of the small amount of HCl improved the accuracy of the flame photometer slightly.

A few words should be said of the methods of analysis used by the Water Resources Laboratory. They use the chlorplatinate method for determination of potassium. They determine sodium by difference, i.e., they determine iron, calcium, magnesium, potassium, carbonate, bicarbonate, sulphate, chloride, fluoride, and silica, and by converting all of these results to equivalents they calculate the sodium content by assuming that there must be enough sodium present to balance the cations and anions. If there should be some metal in the sample for which they did not analyze, then their calculations for sodium would tend to be high. If there should be some acid radical present for which they did not analyze, their results for sodium would tend to be low. It should further be remembered that the accuracy of most quantitative analyses decreases at these very low concentrations; while on the other hand, as has been previously pointed out in this article, the flame photometer seems to have its highest accuracy on concentrations of less than 100 parts per million.

To properly evaluate the accuracy of the flame photometer one should consider the errors reported for various methods that have been proposed. The following are a few such errors reported in the analyses for potassium:

Caley[1] found 2% error on samples containing 5 mg. of potassium in 20 ml. of water, using a volumetric, magnesium uranyl acetate method, and higher percentage error on more dilute samples. Kaye[2] found -4% to +2% error on .02 to .12 mg. in .5 ml. of water, using a cobaltinitrite-ceric sulfate method. Klein and Jacobi[3] found -1% to +.5% error on .1 to .2 mg. in 5 ml. of water, using a cobaltinitrite-ceric sulfate method. Kolthoff and Bendix[4] found -2.2% to +3.5% error on 1 to 20 mg. in 5 ml. of water, using a dipicrylamine method. Robinson and Hauschildt[5] found slightly over 1% error on 8.79 mg. in 35 ml. of water, using a cobaltinitrite method. Smith[6] found -3.5% to +2.4% error on samples containing .0083 g. to .401 g. KCl, using a perchlorate process and a final precipitation in N butyl alcohol. Smith and Gring[7] found not over 5% error on samples of 1 to 3.9 mg., using a perchloric acid-chloroplatinic acid method. Smith and Ross[8] found -.5% to +.15% error on .05 to .24 mg. KCl, using

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[1] Caley, E. R., J. Am. Chem. Soc. 52, pp. 1349-53 (1930).

[2] Kaye, I. A., Ind. Eng. Chem., Anal. Ed. 12, p. 310 (1940).

[3] Klein, B., and Jacobi, M., Ibid. 12, p. 687 (1940).

[4] Kolthoff, I. M., and Bendix, G. H., Ibid. 11, pp. 94-98 (1939).

[5] Robinson, R. J., and Hauschildt, J. D., Ibid. 12, p. 676 (1940).

[6] Smith, G. F., J. Am. Chem. Soc. 45, p. 2073 (1923).

[7] Smith, G. F., and Gring, J. L., Ibid. 55, pp. 3957-61 (1933).

[8] Smith, G. F., and Ross, J. F., Ibid. 47, pp. 1020 (1925).

a perchloric acid method. Smith and Shead[9] found -10% to +2% error on .07 to .31 mg. KCl using a perchloric acid method. In the Fresenius chloroplatinate method they[10] found -.18% to +.37% error. Wander[11] found -2.2% to +1.3% error on 5 mg. K per ml. using a photometric-colorimetric-cobaltinitrite method. Weaver and Lykken[12] found not over 3% error on samples containing from .001% to 3.0% potassium.

As to the accuracy of various methods of determining sodium, the following quotation from Collins' review[13] on the use of uranyl acetate reagents in determination of sodium seems to be typical:

> "The accuracy of the methods used for determining sodium with uranyl acetate reagents has been widely investigated and only by giving some idea of the comparative accuracies of a few of the gravimetric, volumetric, and colorimetric methods can a general idea of the accuracy of the method as a whole be obtained. Because of the difference in precipitating reagents, conditions of precipitation, effects of interfering substances, etc., a true perspective of comparative accuracy does not exist when the methods are applied to technical analysis.
>
> "In the case of gravimetric analyses, Caley found that the highest accuracy exists for small quantities of sodium when small reagent and small volumes are used. Noda, and Jendrassik and Dzicbek found that the error does not exceed ±1% in the presence of various salts, Schoorl showed that an analytical error of 0.25% is possible with Kahane's method but that it can be reduced to 0.1%, Barber and Kolthoff, and Rusznyak and Hatz showed a possible error of ±0.5%, and Bertrand said the error is ±0.3% for high concentrations of sodium and ±2% for small amounts. Petukova said 99.82% of the true sodium content is shown with the uranyl acetate reagent. Sobel, Kraus, and Kramer showed an accuracy of ±0.42% in sodium determination.

---

[9] Smith, G. F., and Shead, A. C., J. Am. Chem. Soc. 54, p. 1722 (1932).

[10] Smith, G. F., and Shead, A. C., Ibid. 53, p. 947 (1931).

[11] Wander, I. W., Ind. Eng. Chem., Anal. Ed. 14, p. 471 (1942).

[12] Weaver, J. R., and Lykken, L., Anal. Chem. 19, p. 372 (1947).

[13] Collins, T. T., Jr., Chem. Eng. News 21, p. 1219 (1943). (A short review only appears in this periodical. The complete article referred to may be obtained in microfilm form from the American Documentation Institute, Washington, D. C.)

"Volumetric methods have been said to be more accurate and sensitive than gravimetric methods because the quantity of water of hydration of the precipitate is not in question and some ions which interfere in the gravimetric procedure do not give erroneous results in this case. Basseja, and Holmes and Kirk found an average error of ±0.5%; the latter down to a concentration as low as 0.023 milligrams of sodium in the sample, while Cheng found a volumetric method to be accurate when the sodium present amounts to 0.04 milligrams. In contrast with these findings, Nikitina had an average error of 6% with 20% variation in his results.

"Colorimetric methods have an error of less than ±1.5% according to Barrenscheen and Messiner, and Sumuleanu and Botezatu and less than 1% according to Darnell and Walker. McCance and Shipp, and Salit showed the sensitivity of their methods to be as low as 0.05 milligrams of sodium but the latter found the error is ±2 or 3% in that extremely low concentration. Tissier and Benard claimed that the colorimetric method checks the gravimetric method within 1 or 2% and is to be preferred because of the saving in time. Smith and Blair said colorimetric analysis for the sodium in water is accurate within ±7 parts per million."

CONCLUSIONS

From the observations made in this investigation, the following conclusions and recommendations are made:

1. Since it was found that the two atomizers did not have the same characteristics, it is feared that no two atomizers furnished by the manufacturer have the same characteristics. It is recommended that anyone using the flame photometer should experimentally determine the air pressure, fuel pressure, and burner jet size which gives the most consistent results with the atomizer to be used. Also, that one should prepare his standard graphs using the same atomizer that is to be used in analyzing the unknowns. The settings found best with the atomizer used in this investigation were an air pressure of 11 pounds per square inch, a fuel pressure equal to atmospheric pressure, plus a pressure of a column of water 17.5 inches high, and a burner jet size of .013 inch in diameter. Using these settings the instrument uses about one-half cubic foot of air per minute (measured at atmospheric pressure), and uses about 2.5 cubic feet of butane per hour (measured at the above mentioned working pressure).
2. Best results seem to be obtained on solutions of less than 100 parts per million concentration; however, more concentrated solutions may be analyzed indirectly by first diluting the solution to a known fraction of its original concentration.
3. Accurate determinations of potassium cannot be made when there is an appreciable amount of tobacco smoke in the air.

It is recommended that the compressed air for the atomizer be filtered through some filter, such as glass wool moistened with motor oil, to remove dust.

4. The height of solution as measured from the end of the atomizer intake tube should be approximately the same when taking all readings.
5. The electrical current furnished to the instrument should be kept at a potential of between 104 and 112 volts.
6. Both burner and electrical circuit should be warmed up for at least one-half hour (preferably an hour) before readings are taken, and the instrument should be re-standardized at least every half hour during operation.
7. Additional knowledge concerning other elements present in the unknown solution must be available in order to know what accuracy may be expected. Certain substances, particularly calcium, barium, magnesium, and strontium, if present in large concentrations, must be removed before using the flame photometer, in order to obtain very accurate results.
8. Using the original galvanometer and the procedure on Pages 26 and 27, one may expect an average error of about 9.25% on sodium determinations and about 7.5% on potassium determinations. By using a more sensitive galvanometer these errors may be cut to 3.5%. These would be the errors to be expected with no interfering substances present.
9. Not counting the time necessary to warm up and standardize the instrument, or the time used in diluting solutions, one

should be able to take the proper reading on a solution in not more than two minutes.

10. It would seem that in case of certain types of samples it may be possible to improve the accuracy of the instrument slightly by addition of sufficient HCl to make the solution about 0.01 M with the acid.

11. As a result of this research, the following topics present themselves as being worthwhile subjects for further investigation:

    a. Possible use of more efficient light filters.

    b. Use of other fuels.

    c. More precise control of air pressure to the atomizer.

    d. Improvement of atomizer.

    e. Absorbtion of light from thermally excited materials by vapor, or heated particles of the same or different material.

    f. Study of other makes and models of flame photometers.

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BIOGRAPHY

John Orlan Wise was born at North River, Virginia, August 10, 1910. He received his grade school education in various public schools of Michigan, West Virginia and Iowa, and was graduated from the public high school at West Branch, Michigan, in June, 1928. The following year he attended Ogemaw County Normal Training class at West Branch, Michigan, upon completion of which he was granted a three-year teaching certificate. The following three years he taught a rural school near Selkirk, Michigan. In September 1932, he entered Central Michigan College of Education at Mt. Pleasant, Michigan, and in June 1935 received a Bachelor of Science Degree and life teaching certificate, with honorable mention for scholarship. For the next several years he had a variety of positions, including three years of teaching in Michigan high schools.

In November 1942, he entered the United States Army, and received an honorable discharge in October 1945. One year of his army service was spent in the European Theater of Operations.

He served as Assistant Instructor in the Department of Chemistry, Oklahoma A. and M. College, for the spring semester and summer term of 1946. In September 1946, he entered the Graduate School, Oklahoma A. and M. College, where he has been employed as a graduate fellow in the Department of Chemistry until the present time. During his graduate fellowship he was also employed on a part-time basis to perform a research project for the Water Resources Division of the U. S. Geological Survey.

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