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THE CHROMOGRAPH, A NEW ANALYTICAL TOOL
FOR LABORATORY AND FIELD USE.

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ABSTRACT

The chromograph, a new device for making confined spot tests on reagent papers, is described. The device is used to confine areas of definite size on a strip of reagent paper fed through the apparatus, and to control automatically the rate of flow of test solution through the confined spot. After a spot test is completed, the sample number may be written on the paper, and the paper pulled through the apparatus to bring into position a spot on an unused portion of the reagent paper for the next test. The strips of paper containing the spots serve as semipermanent records of tests performed. The rate of flow of test solution through the reagent paper is controlled by the pull of a column of water and/or the filtrate from previous tests, and by a capillary tip which decreases the rate to less than that permitted by the reagent paper alone.

Procedures for chromatographic determination of nickel with dimethylglyoxime reagent paper and of copper with rubeanic acid reagent paper are described. The chromograph has been used successfully in locating nickel- and copper-bearing formations by testing samples of the overlying soils.

INTRODUCTION

The use of spot tests for detecting ions in solution has long been known as a technique capable of high sensitivity and specificity. Yagoda (1937) cites the use of such a method by Pliny, as early as 23 to 79 A. D., whereby ferrous sulfate in verdigris was detected by use of papyrus saturated with extract of gall-nuts. In modern qualitative analysis, test papers treated with reagents are extensively used. Feigl's (1942) "Qualitative Analysis by Spot Tests" is perhaps the best-known compilation of such methods.

The spot-test technique consists essentially of bringing reagent and test solution together on paper or other porous medium. The reaction products, concentrated in a small area at the contact of reagent and test solution, are easily detected, and the excess liquid flows away in the surrounding fibers. The spot test may be made by placing a drop of test solution on the paper followed by a drop of reagent solution, the reagent may be put on the paper first followed by the test solution, or reagent solution and test solution may be placed side by side with the reaction products forming at the junction of the two drops. Papers previously coated with reagents also are used extensively. (Feigl, 1942)

As a qualitative technique, spot tests have several advantages over tests made in the usual way in solutions. Colored reaction products concentrate in a small area and are thus easily seen against the white background of the paper. As the solution spreads by capillarity through the paper, reaction products may form in the paper at different distances from the point where the drop was placed, in accordance with differences in solubility. This makes possible the detection of a number of ions in one spot test, as well as making the test for a given ion more specific. Another advantage of the spot test is the speed and ease with which the test may be made with simple and cheap apparatus. Whether the ion is present in large or small amounts also can be seen.

The sensitivity of the spot test is increased by any modification that prevents spreading of the reaction products through the pores of the paper. Hahn (1931) accomplished this by applying the test solution to the reagent paper through the fine tip of a capillary tube, the reaction products concentrating at the point of entry of test solution into the paper. Clarke and Hermance (1937) used this technique to control the speed of flow of test solution onto the reagent paper by the inclination of a capillary burette in a special assembly.

These spot-test techniques serve well the needs of qualitative testing, as they are highly sensitive, specific, and easy to perform. Their application in determining the quantity of an ion present, however, is limited by the fact that the reaction products form in an area of indefinite extent. This exact area is not reproduced in successive tests. In colorimetric determinations the quantity of an ion is found by the intensity of color in a fixed volume of solution of fixed thickness. Similarly, in spot testing the area containing the colored reaction product, the intensity of the

color, and the volume of test solution used must be known in order to determine the quantity of an ion present.

Yagoda (1937) first proposed the use of a confined spot in quantitative spot testing. The spot test was confined within an area of definite size by means of a barrier containing water-repellent material, such as paraffin wax. Yagoda describes equipment needed to impregnate the paper with paraffin and leave spots of definite size for making the spot test. The test was made by placing a measured drop on the confined area containing reagent and drawing the solution through the paper by suction below. The estimate may be made by comparing the color of the confined spot with standards, or, as recommended by Yagoda, by diluting the solution to the point where the color produced in the confined spot is barely visible and matches that of a standard.

In making quantitative spot tests with large volumes of solution, Clark and Hermance (1938) confined the reaction by pressure around apertures above and below the paper. The reagent paper was in the form of a disc placed between apertures and held in a special clamping assembly. They recognized the importance of speed of flow of solution through the confined spot and were able to control this with the large volumes used (250 to 1000 ml) simply by adjusting a stopcock. The present study shows that control of speed of flow is necessary for reproducible results also in small volumes of test solution.

The chromograph (patent applied for) was designed to control the speed of flow and to confine new areas for successive tests quickly and easily. The device confines areas of definite size on a strip of reagent paper fed through the apparatus, and automatically controls the rate of flow of test solution through the confined spot. As each spot test is completed, the sample number, location, or other distinguishing data are written on the paper, and the paper is pulled through the apparatus to bring into position for the next test a spot on an unused portion of the reagent paper. The strips of paper containing the spots serve as semipermanent records of tests performed. The rate of flow of test solution through the confined spot is automatically controlled by the pull of a column of water and/or the filtrate from previous tests, together with a capillary tip to retard the rate of flow. The capillary tip makes the rate of flow essentially independent of the porosity of the filter paper and of the quantity of precipitate on the confined spot.

ACKNOWLEDGMENTS

Details of design of the chromograph were made by Joseph F. Mullins, instrument maker at the Bureau of Plant Industry, U. S. Department of Agriculture. His help and that of Frederick G. Settle, who constructed the chromographs, made this study possible.

Soil samples for the field trial were collected by Charles Milton and H. E. Hawkes. George E. Blandford, Jr., assisted in the analytical work during the field trial.

Laboratory determinations of copper in soils, used in establishing the accuracy and dependability of the field test, were made by Laura Reichen, Frederick Ward, and Hy Almond.

TYPES OF CHROMOGRAPHIC DETERMINATIONS

1. Precipitation reactions.

1a. With reagent papers. The paper is impregnated with a slightly soluble reagent which slowly dissolves, causing the ion sought to be precipitated. The solubility of the reagent must be such as to act as an efficient precipitant without being completely removed during the passage of the solution. The determinations of copper and nickel in soils, to be described, are examples.

1b. With reagent added to the solution. A test for nickel may be made by adding a water solution of sodium dimethylglyoxime to the solution in the chromograph and catching the precipitate on a confined area of untreated filter paper.

1c. Group separations followed by specific tests on the spot. Numerous reagents serve as precipitants for several ions, thus indicating the presence or absence of groups of ions. The resulting spots can then be altered to indicate the quantity of each ion present. For example, rubenic acid precipitates cobalt, nickel, and copper from ammoniacal solution, and such a spot would serve to indicate the presence or absence of all three of these ions. Spots made in this way remove all three ions from solution, and the spots may then be tested for each of these three ions.

2. Alteration of materials on the paper.

The paper contains reagents whose composition and properties are changed by the passage of specific ions. Bleaching of a reagent paper containing zirconium alizarinate by fluoride ion offers possibility of chromatographic application as a test for fluoride.

3. Ion-adsorption technique.

The reagent paper is coated with a material capable of adsorbing certain ions; these ions are fixed on the surface of a confined spot, which then may be tested for a specific ion. Amberlite resin and activated alumina are examples of such materials. Lead ion may be adsorbed in a confined spot on reagent paper containing amberlite resin; the presence of lead in the spot is indicated by the appearance of a red color with potassium rhodizonate solution.

PROPERTIES USED TO COMPARE CONFINED SPOTS

Color is the most obvious property for comparing confined spots in quantitative determinations. Any measurable property of the deposits on the confined spots may be used as means of comparison. As examples, fluorescence, radioactivity, or weight may be the means of measurement or comparison. In addition the confined spot may be used as a means of collecting the ion to be measured, after which the material may be removed from the spot prior to determining the ion by whatever means available.

DETAILED DESCRIPTION OF A CHROMOGRAPH

An assembled chromograph is shown in figure 1 and details of the filter base and filter head are shown in figure 2. The filter base and filter head are Lucite plastic. Filter base and stopcock may be made in one piece if desired.

Dimensions.

In order to make comparable results with different chromographs, certain dimensions were tentatively adopted. The bottom opening of the funnel insert and the hole in the beveled washer were made a quarter of an inch in diameter, thus producing a confined spot of that size. The drain tube through the filter-base body also was made a quarter of an inch in diameter, and, for purposes of timing and adjusting, marks a quarter of an inch apart were placed on the outside of the filter-base body, as shown in figure 1, the upper mark being a half inch below the top of the beveled washer when placed in the washer seat. The drain tubes leading to the capillary tip are sufficiently large to allow the free flow of liquid. The outlet of the capillary tip was placed 9 inches below the upper timing mark.

Assembling the apparatus.

Screw the filter-base adaptor into the filter-base body to make a liquid-tight connection (see figure 2). Insert the beveled washer in the washer seat of the filter-base body, beveled edge up. Assemble the funnel head by inserting the funnel insert (screw section up) into the pressure flange (screw section down), and screw the funnel insert screw cap tightly onto the top of the funnel insert. The parts of the funnel head are constructed with sufficient clearance so that the funnel insert turns freely in the pressure flange when the filter head is assembled. Next screw the filter head into the top of the filter-base body.

Connect the 3-way stopcock to the filter-base adaptor and the standard capillary tip to the outlet tube with rubber tubing. Connect the adjustor bulb to the adjustor-bulb tube, as shown in figure 1.

Selection or adjustment of capillary.

The time of drainage tentatively adopted was 200 ± 10 seconds for the top of a column of solution to fall from the upper timing mark to the lower with a 9-inch head of solution, and without paper in the reagent paper slot. In order to attain this it was necessary to select or adjust the capillary. A 2-inch capillary of 0.15 mm internal diameter was found to meet these requirements for drainage time. Capillaries of larger bore could be used by drawing the tube out in the flame, and pinching off the tapered end bit by bit until the proper drainage time was attained. Capillaries that were of slightly smaller bore could be adjusted to the proper drainage time by shortening in a like manner.

Filling the apparatus.

Before use, the outlet tube, capillary, adjustor-bulb tube, and adjustor bulb are filled with water.

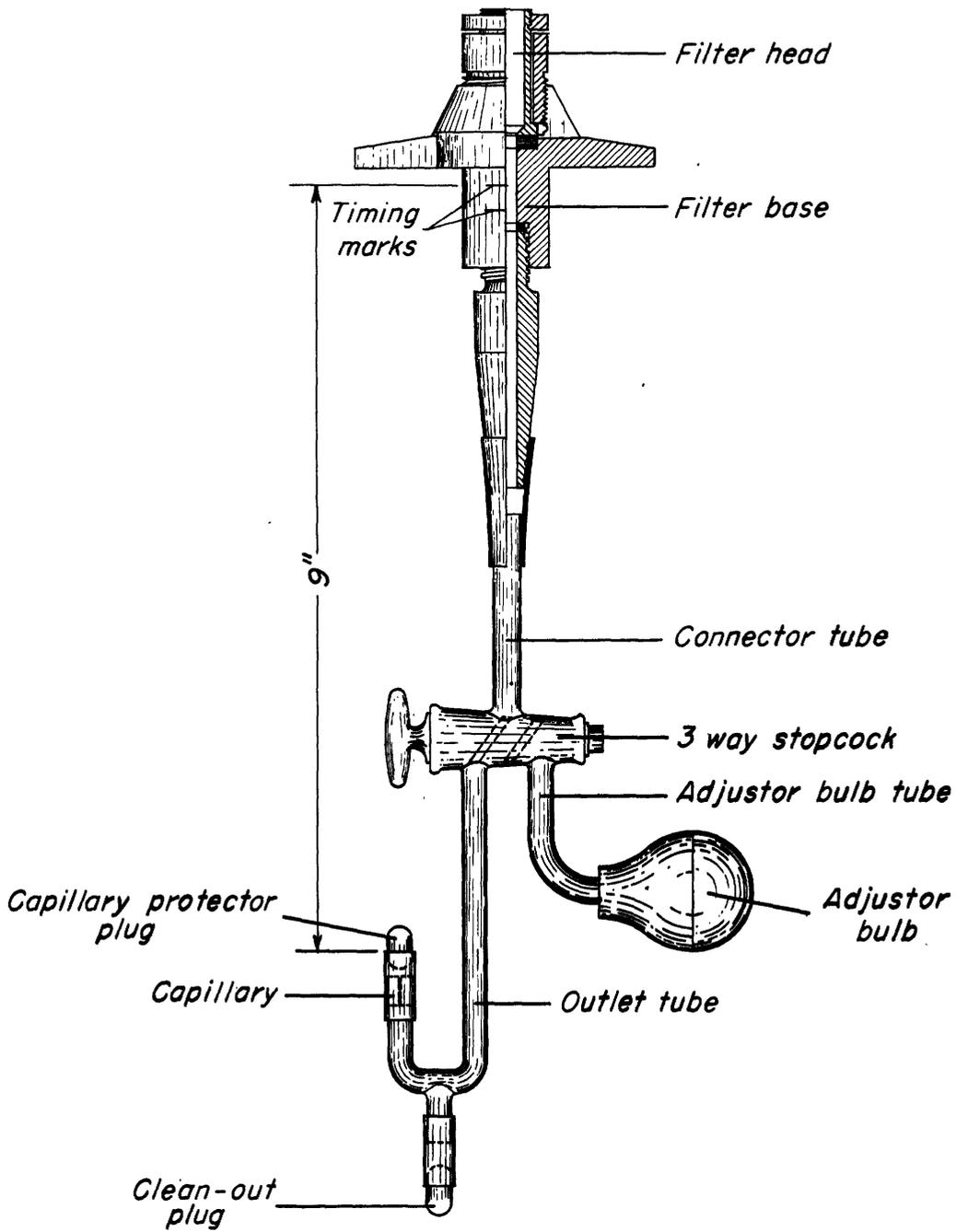


Figure 1. The chromatograph assembled

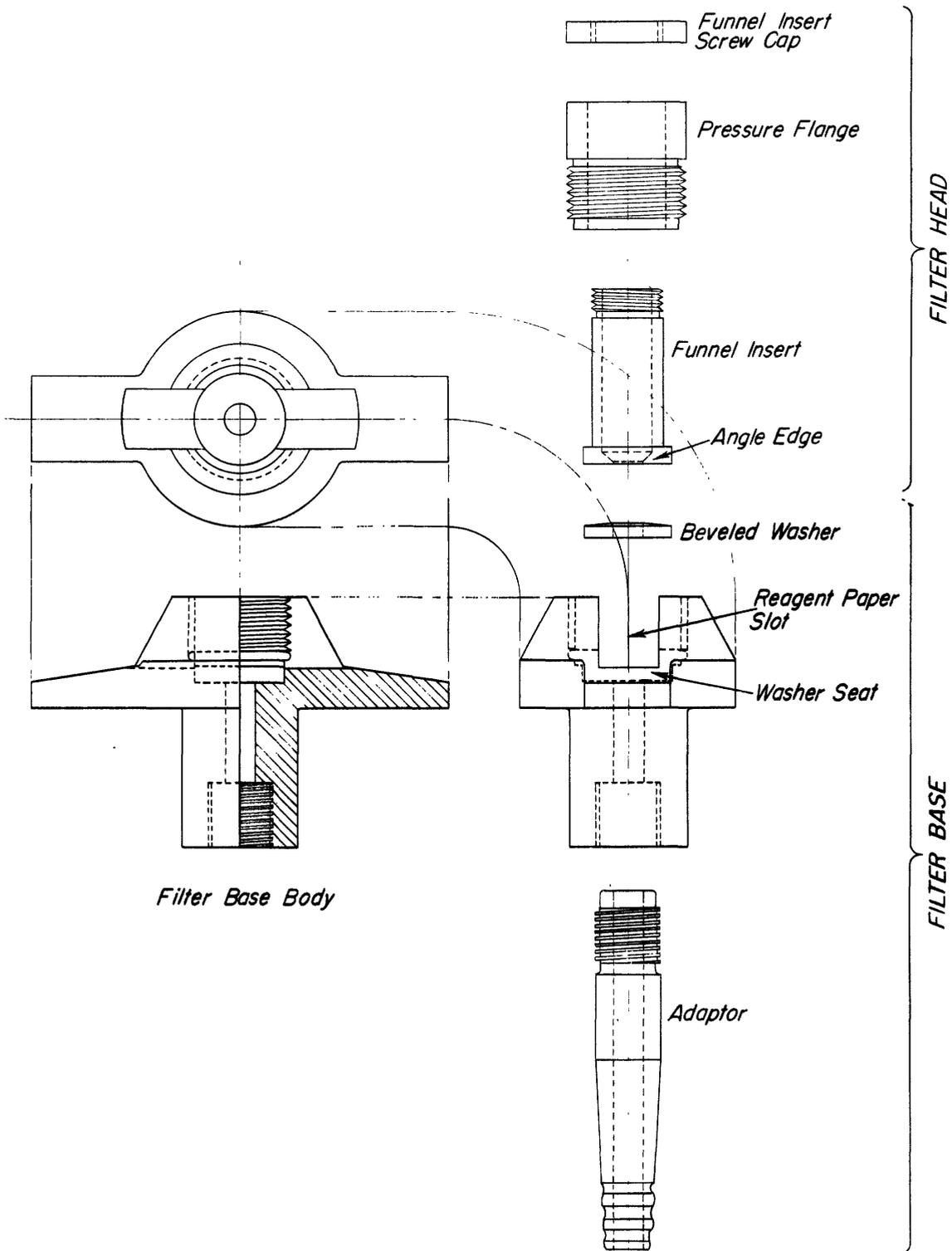


Figure 2. Parts of filter base and filter head of chromatograph

EFFECT OF SPEED OF FLOW

The intensity of color on the confined spot has been shown by Clarke and Hermance (1938) to be affected by the speed of flow of the test solution through the reagent paper. A simple automatic device for keeping the speed of flow of the solution fairly constant was therefore embodied in the chromograph.

The effect of speed of flow in chromographic tests for nickel with dimethylglyoxime reagent paper is shown in table 1. In these tests, the capillary tip was removed from the chromograph and the speed of flow was varied by increasing or decreasing the column of water in the tube below the reagent paper. The results in table 1 were obtained by comparing the test spots with standard spots prepared as described later, under the procedure for nickel. A decrease of yield of nickel can be seen with increasing speed of flow, corresponding to increase in the length of water column used. Results in table 1 are all low because the rate of flow was excessively fast and also because of the absence of modifier ions, discussed in the following section; the decrease in yield with increased rate of flow is clearly indicated.

The effect of the suction provided by 2-inch and 8-inch columns of water, without capillary, for the copper test is shown in table 2. The spots are compared with standard spots prepared or described later under the procedure for copper. The time required for the solutions to pass through the paper is given in the second column.

With a 2-inch water column fairly satisfactory spots were obtained for very low concentrations. However, at a concentration of 3.16 micrograms of copper per milliliter, the paper became clogged with precipitate and more than twelve minutes was required for passage of 0.2 ml of the solution through the test paper.

The 8-inch water column was much too fast for solutions of low concentrations, and adequately fast for solutions of high concentration.

An inspection of these data leads to the following conclusions: (1) The rate of flow must be slow enough to permit essentially complete precipitation of the test ion; (2) the effective suction must be great enough to pull all of the test solution through the paper in a reasonable period of time; (3) the reaction of the test ion with the reagent in the paper forms a precipitate which decreases the effective porosity of the paper. From these considerations it becomes evident that the rate of flow must be reasonably independent of changes in the porosity of the test paper. This, we believe, is attained by use of a 9-inch column of water below the test paper to give an adequate suction capacity; the rate of application of the suction is controlled by a capillary of sufficiently small bore to allow 0.2 ml of solution to flow through the capillary in 200 seconds. With this system, solutions very low (0.26 microgram per milliliter) in copper require 250 seconds for passage through the test paper, whereas solutions of the maximum concentration used (42.0 micrograms per milliliter) require only 360 seconds for passage.

Table 1.—Effect of speed of flow of solution on chromographic tests for nickel (0.2 ml of solution was used in test. Capillary tip was omitted. Modifier ions were present in standard spots but not in test spots.)

| 10 gammas of Ni per ml taken | | | | 75 gammas of Ni per ml taken | | | |
|------------------------------|--------------------------------------|----------------------|------------------|------------------------------|--------------------------------------|----------------------|------------------|
| Head of Water (inches) | Time to Flow through Paper (seconds) | Ni Found (gammas/ml) | Percent of Error | Head of Water (inches) | Time to Flow through Paper (seconds) | Ni Found (gammas/ml) | Percent of Error |
| 2 | 90 | 2.4 | -76 | 2 | 202 | 35 | -53 |
| 2 | 80 | 2.0 | -80 | 2 | 203 | 35 | -53 |
| 2 | 110 | 2.4 | -76 | 2 | 174 | 30 | -60 |
| 2 | 92 | 2.0 | -80 | 2 | 158 | 30 | -60 |
| 3 | 50 | 1.7- | -83 | 3 | 129 | 30 | -60 |
| 3 | 47 | 1.0 | -90 | 3 | 170 | 30 | -60 |
| 3 | — | 1.5 | -85 | 3 | 148 | 30 | -60 |
| 3 | — | 1.2 | -88 | 3 | 188 | 30 | -60 |
| 6 | 26 | .8 | -92 | 6 | 43 | 20 | -73 |
| 6 | 19 | .7 | -93 | 6 | 34 | 20 | -73 |
| 6 | 26 | .8 | -92 | 6 | 38 | 20 | -73 |
| 6 | 28 | 1.0 | -90 | 6 | 37 | 20 | -73 |
| 12 | 8 | .2 | -98 | 12 | 15 | 15 | -80 |
| 12 | 8 | .2 | -98 | 12 | 12 | 15 | -80 |
| 12 | 8 | .2 | -98 | 12 | 15 | 15 | -80 |
| 12 | 8 | .2 | -98 | 12 | — | 15 | -80 |

Table 2.—Effect of speed of flow of solution on chromatographic tests for copper (0.2 ml of solution was used in test. Capillary tip was omitted. Modifier ions were present in standard spots but not in test spots.)

| Head of Water (inches) | Time to Flow through Paper (seconds) | Cu Content of Solution (gammas/ml) | Cu Found (gammas/ml) | Percent of Error |
|------------------------|--------------------------------------|------------------------------------|----------------------|------------------|
| 2 | 186 | 0.56 | 0.4 | -29 |
| 2 | 210 | .75 | 1.2 | +60 |
| 2 | 150 | 1.00 | 1.2 | +20 |
| 2 | 181 | 1.33 | 1.4 | + 5 |
| 2 | 151 | 1.78 | 1.6 | -10 |
| 2 | 231 | 2.37 | 3.0 | +27 |
| 2 | 744 | 3.16 | 6.0 | +90 |
| 8 | 75 | .56 | .4 | -29 |
| 8 | 54 | .75 | .4 | -47 |
| 8 | 54 | 1.00 | .4 | -60 |
| 8 | 45 | 1.33 | .8 | -40 |
| 8 | 47 | 1.75 | 1.2 | -31 |
| 8 | 42 | 2.37 | 1.3 | -45 |
| 8 | 54 | 3.16 | 2.4 | -24 |
| 8 | 51 | 4.22 | 3.2 | -24 |
| 8 | 51 | 5.62 | 3.6 | -36 |
| 8 | 105 | 7.50 | 6.0 | -20 |
| 8 | 248 | 10.00 | 12.0 | +20 |
| 8 | 248 | 13.30 | 18.0 | +35 |
| 8 | 270 | 17.80 | 24.0 | +35 |
| 8 | 270 | 23.70 | 24.0 | + 1 |
| 8 | 276 | 31.60 | 44.0 | +39 |
| 8 | 264 | 42.20 | 44.0 | + 4 |

MODIFIER IONS

Preliminary results with the chromatograph were disappointing because the effect of other ions on the intensity of colors was not fully considered. Other ions which are not themselves precipitated by the reagent have marked effects on the colloidal dispersion and, therefore, the filterability of the precipitates formed. Ions that increase or decrease the color obtained on the spot are those with high valences such as ferric iron, aluminum, and titanium. Even the small quantity of silicon derived from the test tube in which the bisulfate fusion was made was sufficient to increase the precipitation of nickel dimethylglyoxime.

Results obtained by comparing the test spots for nickel with a standard spots made in the absence of modifier ions and with those made in the presence of modifier ions obtained

from soil are shown in table 3. The tests were made on standard mixtures of nickel-bearing laterite and garnierite diluted with quartz, orthoclase, and calcite. The results in table 3 show that test on solutions containing these ions should be compared only to standards prepared from solutions of similar composition, not solutions containing nickel alone.

The effect of modifier ions on the test for copper with rubeanic acid reagent paper is shown in table 4. These ions had an inhibiting action on the precipitation of copper rubeanate, and when they were present a less intense color was obtained. For this reason, when the standard comparison spots were made in the absence of these modifier ions, results of tests on soil samples were low, frequently by more than 50 percent of the copper present, as shown in table 4.

Table 3.—Results of comparing nickel dimethylglyoxime test spots with standard spots made with and without modifier ions present

| Nickel Present (parts per million) | Nickel Found (parts per million) | |
|------------------------------------|--|---|
| | Compared with Standard Spots Made with Modifier Ions Present | Compared with Standard Spots Made from Pure Nickel Solution |
| 77 | 75 | 160 |
| 85 | 70 | 200 |
| 92 | 70 | 200 |
| 160 | 150 | 400 |
| 170 | 220 | 400 |
| 170 | 200 | 400 |
| 180 | 220 | 500 |
| 390 | 400 | 800 |
| 400 | 450 | 1200 |
| 480 | 600 | 1200 |
| 500 | 450 | 1100 |
| 680 | 900 | 1600 |
| 680 | 700 | 1600 |
| 880 | 1000 | 2200 |
| 920 | 900 | 2200 |
| 2500 | 1700 | 2800 |
| 2700 | 2000 | 3000 |
| 3300 | 2500 | 3000 |
| 3400 | 2500 | 3800 |

Table 4. —Results of comparing copper rubeanate test spots with standard spots made with and without modifier ions present

| Copper Present (parts per million) | Copper Found (parts per million) | |
|---------------------------------------|---|--|
| | Compared with Standard Spots Made with Modifier Ions Present | Compared with Standard Spots Made from Pure Copper Solution |
| 60 | 80 | 30 |
| 120 | 100 | 80 |
| 120 | 80 | 30 |
| 120 | 150 | 60 |
| 200 | 180 | 60 |
| 200 | 250 | 90 |
| 200 | 150 | 80 |
| 380 | 400 | 360 |
| 410 | 350 | 280 |
| 650 | 550 | 200 |
| 1000 | 1000 | 600 |

EXAMPLES OF THE USE OF THE APPARATUS FOR DETERMINATION OF COPPER AND NICKEL IN SOILS

Preparation of reagent papers. Large quantities of the reagent papers may be prepared and stored for future use.

1. Dimethylglyoxime reagent paper. With an atomizer spray a one-percent solution of dimethylglyoxime in alcohol onto Whatman No. 50 filter paper, applying just enough of the solution to fill the pores of the paper. Avoid localized excesses of the solution, as uneven distribution of the reagent results when the solution spreads by capillarity through the paper. Make three applications of the solution, allowing the paper to dry after each application. Dry the paper and cut into strips 7/16 inch in width.

2. Rubeanic acid reagent paper. Prepare in the same way as the dimethylglyoxime paper, using a one-percent solution of rubeanic acid in alcohol.

Preparation of standard spots. The colors obtained on the confined spots are affected by the presence of modifier ions in the solution, such as iron and aluminum, as previously explained. It is therefore necessary to prepare the standard spots used for comparison, not from solutions that contain copper or nickel alone, but from solutions that contain the ions that will be present in the unknown solutions to be analyzed.

Soil solution: Fuse in Pyrex beaker 7 g. of soil, selected for exceedingly low copper and nickel content, with 35 g. of potassium bisulfate. Cool, add 27 g. of sodium citrate and 100 ml. of distilled water, and digest on the steam bath until the cake is disintegrated. Cool, dilute to 200 ml., and filter through Whatman No. 50 filter paper.

Standard nickel and copper test solutions: Prepare a series of standard nickel and copper test solutions by adding appropriate volumes of standard solutions of these metals from a microburette to 3 ml. of the soil solution. Add NH_4OH until a piece of red litmus paper in the solution turns blue. Dilute to 5 ml. The series of nickel test solutions should vary from 40 gamma Ni/ml. (corresponding to 2000 p.p.m. Ni in 0.1 g. of soil sample) to 0.30 gamma Ni/ml. (corresponding to 15 p.p.m. Ni in 0.1 g. of soil sample) and the series of copper test solutions should vary from 30 gamma Cu/ml. to 0.20 gamma Cu/ml. Dilute the copper test solutions by adding 1 ml. of 1-to-1 acetic acid so that they contain from 26.7 gamma Cu/ml.

(corresponding to 1500 p.p.m. Cu in 0.1 g. of soil sample) to 0.167 gamma Cu/ml. (corresponding to 10 p.p.m. Cu in 0.1 g. of soil sample). The nickel and copper contents of the standards in the series should be made so that successive standards differ by about 30 percent.

Make confined spot tests with 0.2 ml. of each of the standard test solutions, using dimethylglyoxime reagent paper for the nickel test solutions, and rubeanic acid reagent paper for the copper test solutions. Mount the series of spots on the edge of a cardboard chart and cover with cellophane tape. Label each spot with the figure of parts per million of Ni or Cu to which it corresponds.

Preparation of sample solution. Fuse 0.1 g. of soil with 0.5 g. of KHSO_4 in a test tube until a dull-red quiescent melt is obtained. As the tube cools, revolve it to allow the molten material to crystallize in a thin layer on the walls of the tube. To the cooled tube add 3 ml. of 13.3 percent sodium citrate solution and boil until the lumps of KHSO_4 disintegrate. Cool, add concentrated NH_4OH until a piece of red litmus paper turns blue, and dilute to 5 ml. with water. Divide the solution in half (one half for determining nickel and the other half for determining copper). Filter one portion for nickel.

Determination of nickel. Place a strip of dimethylglyoxime reagent paper in the reagent-paper slot of a chromograph. With the stopcock turned to connect the adjustor bulb with the connector tube, press the rubber adjustor bulb to force the water up the tube to the upper timing mark, then close the stopcock. Turn the pressure flange to press the reagent paper tightly between the funnel insert and the beveled washer. Place 0.2 ml. of the filtered solution for the nickel test in the bottom of the funnel insert. Turn the stopcock to join the connector tube with the outlet tube. When all of the solution has drained through the reagent paper, turn the stopcock to join the adjustor bulb to the connector tube. Raise the filter head by turning the pressure flange and allow the liquid column together with the test solution (from which the nickel has been removed) to be drawn down into the adjustor bulb. Raise the filter head sufficiently high so that the bottom of the funnel head is well clear of the reagent paper. Draw the reagent-paper strip through the reagent-paper slot until the spot is clear of the filter head, and write the sample number on the reagent paper below the spot. Readjust the liquid column

to the level of the upper timing mark and proceed as before with the next solution to be tested for nickel. When the spots containing the red nickel dimethylglyoxime are dry, compare them with the chart containing spots made with known quantities of nickel.

Determination of copper. To the 2.5 ml. of solution set aside for copper, add 0.5 ml. of 1-to-1 acetic acid. Filter. Make a confined-spot test with 0.2 ml. of this solution in another chromograph containing rubeanic acid reagent paper in the manner described for the nickel determination, and compare the spots when dry with the chart of standard copper rubeanate spots.

Storage of test spots. When dry, place the strip of reagent paper containing the test spots on a slightly longer piece of cellophane tape, with spots face down against the adhesive, and mount the strip on a page of the notebook. Spots stored in this way have undergone no apparent changes in six months, other than a slight browning of the paper.

EXPERIMENTAL RESULTS

Results obtained in the chromatographic determination of nickel and copper are given in table 5. For nickel three samples were studied which had been analyzed by D. Smith and R. Nordgren, reported by Sandell and Goldich (1943) together with a large number of standard mineral mixtures of known nickel content containing garnierite and laterite. Chromatographic tests were made for copper on soils previously analyzed for copper by the dithizone method of Holmes (1945).

Most of these results are accurate to within 30 percent of the element determined (26 out of 38 for nickel, and 27 out of 38 for copper fall within this limit), showing that the device is capable of yielding useful information in the field. This fact is further illustrated by results in the next section.

The confined spot obtained with a chromatograph measures only the amount of the element dissolved in the attack of the sample. The method as outlined did not give good results for nickel on lavas from Hawaii, apparently because of failure of the bisulfate fusion to dissolve all of the nickel.

Table 5.—Analyses for nickel and copper by the chromatographic method

| Type of Material | Nickel (parts per million) | | Percent of Error | Type of Material | Copper (parts per million) | | Percent of Error |
|----------------------------------|----------------------------|-------|------------------|------------------|----------------------------|-------|------------------|
| | Taken | Found | | | Taken ^{b/} | Found | |
| Basalt | 70 _{a/} | 30 | - 57 | Soil | 11 | 10 | - 9 |
| Basalt | 70 _{a/} | 30 | - 57 | | 14 | 50 | +260 |
| Laterite + calcite | 77 | 75 | - 3 | | 18 | 20 | + 11 |
| Garnierite + orthoclase + quartz | 85 | 70 | - 18 | | 20 | 10 | - 50 |
| Garnierite + quartz + calcite | 92 | 70 | - 24 | | 20 | 10 | - 50 |
| Laterite + orthoclase | 110 | 150 | + 36 | | 35 | 60 | + 71 |
| Laterite + orthoclase | 110 | 220 | +100 | | 45 | 45 | 0 |
| Basalt | 120 _{a/} | 100 | - 17 | | 60 | 60 | 0 |
| Basalt | 120 _{a/} | 100 | - 17 | | 60 | 80 | + 33 |
| Basalt | 120 _{a/} | 90 | - 25 | | 60 | 80 | + 33 |
| Garnierite + orthoclase + quartz | 180 | 150 | - 6 | | 78 | 140 | + 80 |
| Laterite + orthoclase | 170 | 200 | + 18 | | 120 | 120 | 0 |
| Garnierite + quartz + calcite | 170 | 220 | + 29 | | 120 | 90 | - 25 |
| Laterite + calcite | 180 | 220 | + 22 | | 120 | 130 | + 8 |
| Basalt | 290 _{a/} | 220 | - 24 | | 120 | 130 | + 8 |
| Basalt | 290 _{a/} | 240 | - 17 | | 120 | 80 | - 33 |
| Basalt | 290 _{a/} | 240 | - 17 | | 120 | 150 | + 25 |
| Garnierite + orthoclase + quartz | 390 | 400 | + 3 | | 120 | 90 | - 25 |
| Garnierite + quartz + calcite | 400 | 450 | + 13 | | 180 | 130 | - 28 |
| Laterite + orthoclase | 480 | 900 | + 88 | | 200 | 150 | - 25 |
| Laterite + orthoclase | 480 | 600 | + 46 | | 200 | 250 | + 25 |
| Laterite + calcite | 500 | 450 | - 10 | | 200 | 250 | + 25 |
| Garnierite + quartz + calcite | 680 | 700 | + 3 | | 310 | 300 | - 3 |
| Garnierite + orthoclase + quartz | 680 | 900 | + 32 | | 310 | 200 | - 36 |
| Laterite + orthoclase | 880 | 1000 | + 14 | | 380 | 600 | + 58 |
| Laterite + calcite | 920 | 900 | - 2 | | 380 | 400 | + 5 |
| Garnierite + orthoclase + quartz | 970 | 1500 | + 55 | | 410 | 300 | - 27 |
| Laterite + orthoclase | 2500 | 1700 | - 32 | | 410 | 350 | - 15 |
| Laterite + calcite | 2700 | 2000 | - 26 | | 410 | 300 | - 27 |
| Laterite + orthoclase | 2900 | 3000 | + 3 | | 410 | 320 | - 22 |
| Laterite + calcite | 2900 | 4000 | + 38 | | 590 | 650 | + 10 |
| Laterite + calcite | 2900 | 4000 | + 38 | | 600 | 850 | + 42 |
| Laterite + orthoclase | 2900 | 3500 | + 21 | | 650 | 550 | - 15 |
| Garnierite + orthoclase + quartz | 3300 | 2500 | - 24 | | 650 | 500 | - 23 |
| Garnierite + quartz + calcite | 3400 | 2500 | - 26 | | 800 | 600 | - 25 |
| Garnierite + orthoclase + quartz | 3600 | 3000 | - 17 | | 880 | 1000 | + 25 |
| Garnierite + orthoclase + quartz | 3600 | 2200 | - 39 | | 1000 | 1000 | 0 |
| Garnierite + calcite + quartz | 3600 | 4000 | + 11 | | 1000 | 1200 | + 20 |

a/ Colorimetric results by D. Smith and R. Nordgren, reported by Sandell and Goldich (1943).
b/ Laboratory results of Laura Reichen, Hy Almond, and Frederick Ward by dithizone method of Holmes (1945).

FIELD TRIALS OF THE CHROMOGRAPH

To discover unforeseen difficulties in the field use of the chromograph and to illustrate its use in locating hidden geological features, one day was spent in a field trial of the apparatus. No operational difficulties were encountered.

Samples of residual soil over a serpentine body high in nickel and a small copper deposit in Fairfax County, Va., were collected and tested for both copper and nickel. Wherever possible the subsoil was sampled at a depth of 1 to 2 feet by means of a light soil auger. Samples were brought to the field station for testing, and the resulting spots mounted in a notebook for later study.

Figure 3 shows the data on the copper content of soil as related to copper-stained Triassic sandstone cropping out about 20 feet north of the zero point on the traverse line. The copper apparently follows a fault striking approximately north. Background values were

about 10 parts per million, whereas near the copper-bearing outcrop, values were as high as 1000 parts per million.

Figure 4 shows results of tests for nickel on soil collected along a line normal to a serpentine dike. Inasmuch as the dike rock was strongly magnetic, its exact location could be established by magnetic dip-needle observations. The correspondence in location of the serpentine between soil tests and magnetic observations is seen to be good except for station 800E, presumably where limits of the nickel-rich soil have been displaced slightly to the west as a result of soil creep. Nickel in the soil east of the serpentine dike averaged 160 parts per million (six trials showed a low of 150 parts per million and a high of 170 parts per million); nickel in the soil west of the dike averaged 62 parts per million (three results were 35, 50, and 100 parts per million). Soil over or immediately adjacent to the serpentine dike contained from 500 to 5000 parts per million of nickel.

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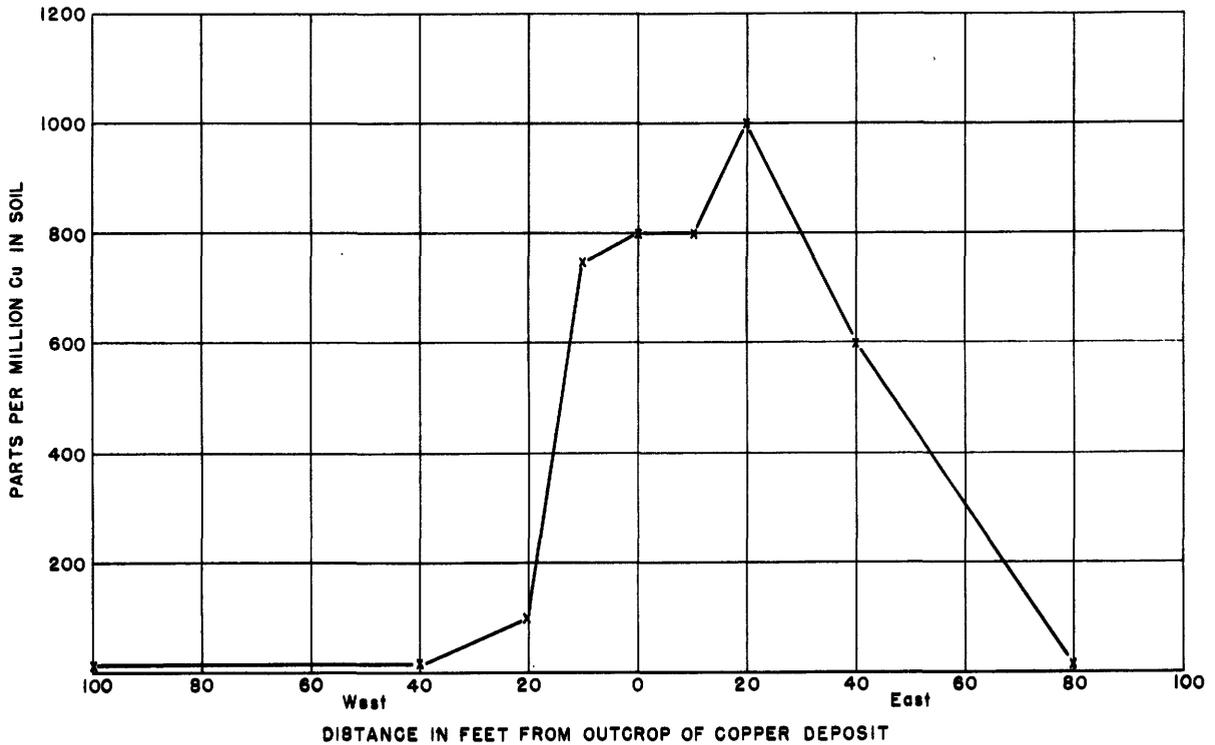


Figure 3. Copper tests on soils near a small copper deposit 0.8 mile east of Chantilly, Fairfax County, Va., on U. S. Highway 50

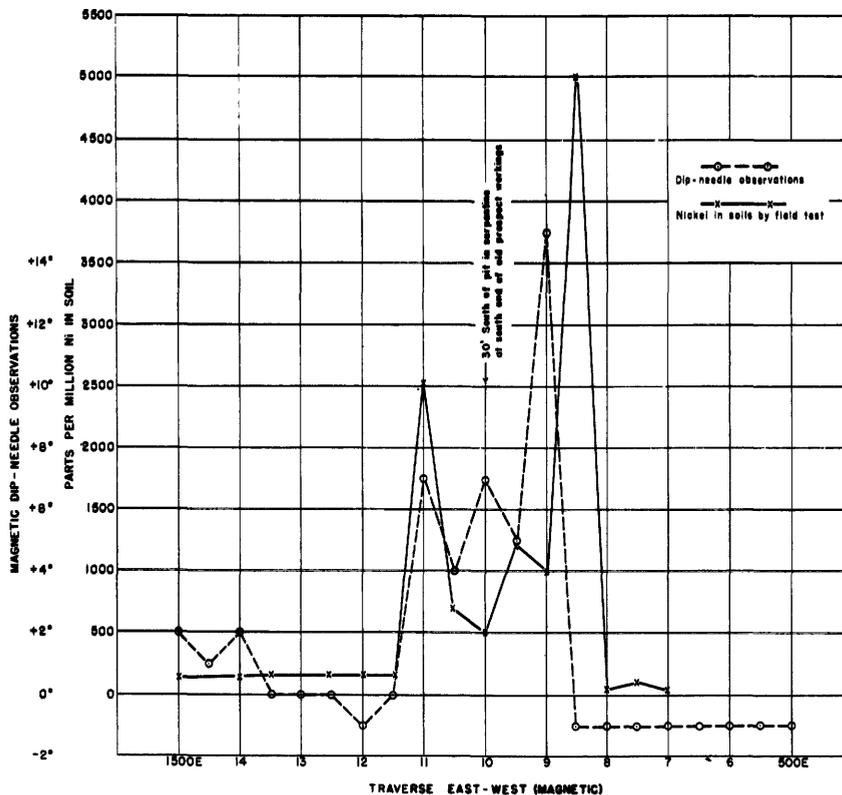


Figure 4. Correlation of magnetic dip-needle observations and nickel tests on soil on traverse across serpentine (Jenkins farm, 1.5 miles southeast of Dranesville, Va., on U. S. Highway 7. Dip-needle readings were made by Charles Milton.

