Soil sampling at the Star mine, Coeur d'Alene district, Idaho

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SOIL SAMPLING AT THE STAR MINE,
COEUR D'ALENE DISTRICT, IDAHO

by

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ABSTRACT

A geochemical prospecting project, by soil sampling, was carried out over the Star mine to test certain methods and their usefulness in the area. The tests employed were the heavy metals test, lead test, and zinc test.

The Star mine is a leading zinc and lead producer. It is located in a steeply dipping shear zone in pre-Cambrian Belt Series quartzite. Ore extends from near the surface to a known depth of 6500 feet below.

The scarcity of surface evidence of mineralization, the general presence of a residual soil mantle which conceals the bedrock, and the high cost of usual exploration methods make this a good test district for soil sampling.

The principles and processes of geochemistry important to soils and soil sampling are discussed.

Soil assay maps and cross-sections of the vein with the assays plotted graphically illustrate and compare the effectiveness of the three tests. The data indicate that the heavy metals test is more useful in this area than the zinc test. While the heavy metals test is suitable for reconnaissance work, the lead test more or less pinpoints the ore structure.
Sampling of the uppermost six inches of soil provided assays which were reliable indicators of bedrock geology, and deeper sampling was unnecessary.

The background counts were found to be 60 parts per million for heavy metals, 50 for zinc, and 30 for lead. The highest assay encountered was 12,000 parts per million (1.2%) of heavy metals. The geochemical halo created by the Star ore body is clearly defined.

The field and laboratory methods used, as well as special problems are discussed. Descriptions and interpretations of the maps and cross-sections illustrating the results of the project are submitted.

Cross-sections and overlays of the plan maps reveal the close correlation of soil assays with the topography and known geology.

INTRODUCTION

Geochemical prospecting, while so new that the techniques are still somewhat experimental, is rapidly becoming recognized as a valuable tool in aiding the prospector in the search for ore deposits, especially in regions where the bedrock is concealed by a blanket of soil.

Involving both geology and chemistry, geochemical prospecting is the searching for surface or near surface chemical anomalies in soil, rock, water or vegetation, which will indicate the presence of a concealed ore body.

In principle, geochemical prospecting is comparable to that of locating a gold lode by panning stream material upstream to the source.
of the metal. Numerous experiments and test projects have proved that the weathering and dispersion of the vein minerals produce chemical anomalies in the overlying soil. The limits of the anomalous areas can be determined by sampling, and when plotted on maps the information may reveal new discoveries or aid in defining the limits of known ones.

In this paper, the term halo refers to the three dimensional zone containing materials derived from an ore deposit and in amounts sufficient to produce a geochemical anomaly in the enclosing rock or soil.

The intensities of the anomalies resulting from "contamination" of the soil through dispersion of the weathered veins depend upon the thickness of the overburden, amount of rainfall, solubility of the minerals, topography, and other factors.

The basis of geochemical work lies in the detection and measuring of minute amounts of metals in the material being sampled. The quantities measured are so small that they are reported in parts per million rather than percentages. It has been found that the ratio of the metal content of the anomalous areas may be several hundred times that of the background count. Background count refers to the average metal content of the normal soil in the general area, and it may vary greatly in different districts.

Requirements of the techniques employed are that they be rapid, sufficiently sensitive and accurate, and economical. These requirements exist because the success of the method depends upon the coverage of
large areas, the analysis of hundreds or perhaps thousands of samples, and the necessity of the laboratory work keeping abreast of the field work.

Since geochemical anomalies are relative, the absolute metal content of the sample is not very important. When a large number of samples are analyzed and the chemical procedure provides consistency of metal extraction, most anomalies can be detected; even though only a fraction of the true metal content is measured. The U. S. Geological Survey considers the maintenance of 30 percent accuracy as being practical.¹

The indicator material for which analysis is made may not be one of the economic metals, but an associated element which may serve as well as a guide and which may produce a more definite geochemical anomaly. In some cases, a more reliable chemical test may exist for an associated element.

After viewing the results of test projects completed by the U. S. Geological Survey, Robert E. Sorenson, Vice President and Chief Engineer and Geologist of the Hecla Mining Company, instigated a soil sampling program which was carried out in the summer and fall of 1951. The area investigated involved one and a half square miles in the vicinity of the Star mine. The field work, map construction, and interpretation of the analyses were done by the writer. The samples were analyzed at the Hecla assay office, Gem, Idaho.

¹ Kennedy, Vance, oral communication.
ACKNOWLEDGEMENTS

The writer gratefully acknowledges the suggestions and encouragement received from Robert E. Sorenson of the Hecla Mining Company in the preparation of this thesis. Sincere appreciation is due the directors of the Hecla, Sullivan, and Coeur d'Alene Syndicate mining companies who made it possible for the writer to use the material obtained while employed by the Hecla Mining Company.

Recognition is due the Hecla assayers, Norman Sather, James Hunter, and Robert Squires for their high quality work in making the soil analyses.

HISTORY OF THE COEUR D'ALENE DISTRICT

Idaho is the leading state in silver production, and is the second largest producer of both lead and zinc. This state also markets substantial quantities of copper, gold, tungsten, and antimony. The Coeur d'Alene district produces over 90 per cent of Idaho's total mineral wealth.

The Coeur d'Alene region was first prospected in 1878, and the town of Murray soon developed near the gold lode and placer deposits on the North Fork of the Coeur d'Alene River. In 1884 the silver and lead mines along the South Fork, in the vicinities of Burke, Mullan, Kellogg, and Pine Creek were discovered.

After the completion of railroads and smelters and the subsequent labor troubles during the 1890's, many of the early discoveries were developed into such famous mines as the Bunker Hill and Sullivan,
Morning, Star, Sunshine, Hecla, and Polaris. New discoveries are still being made by deep exploration.

The history of the Star Mine is associated with that of the Morning Mine, because the Star ore body is the westerly extension of the Morning lode (See Fig. 7). This area was first mined through the Morning Mine, which was first worked systematically in 1887. The Morning Mine was purchased by the Federal Mining and Smelting Company in 1905. The underground work was extended beneath the Star claims, and long, expensive litigation resulted. Later, the Sullivan Mining Company became the owner of the Star Mine and developed it by crosscutting 9,100 feet from the Hecla Mine shaft at Burke and by raising and sinking near the Star ore body. The Star winze has reached a depth of 6,100 feet below the surface.

GEOGRAPHY AND PHYSIOGRAPHY

The Coeur d'Alene Mining District occupies an area of about 30 miles extending west from the Idaho-Montana border and 15 miles from north to south, in the Panhandle of Northern Idaho. It lies in the Coeur d'Alene Mountains, which are a part of the Rocky Mountain physiographic province. Many of the peaks have elevations between 6,000 feet and 6,500 feet and display cirques and U-shaped valleys resulting from alpine glaciation. The maximum relief is about 4,000 feet. Extensive dissec-

Plate 1. View showing topography of the Coeur d'Alene district. Looking west from U. S. 10, about five miles east of Mullan, Idaho.
tion of the region by erosion has resulted in sharp ridges and precipitous slopes.

The region is covered by a heavy growth of timber and brush, except where outcrops have formed talus slides. Rain and snowfall is heavy, the annual precipitation being 38 inches.

The principal rivers of the district are the North and South Forks of the Coeur d'Alene River, which combine and drain westward into Coeur d'Alene Lake and thence into the Spokane and Columbia Rivers.

The main industries are mining, smelting, and lumbering. The district is accessible by U. S. Highway 10, and is served by the Union Pacific and Northern Pacific Railways. Within the district are the towns of Murray (north of map area), Wallace, Burke, Mullan, Kellogg and Osburn. (See Fig. 2)

GEOLOGY

Stratigraphy

Beltian Series

The sedimentary rocks of the district include about 20,000 feet of shallow water deposits. These consist of shale, quartzite, argillite, and impure calcareous rocks, belonging to the pre-Cambrian Belt series. The series has been regionally metamorphosed and locally altered by sericitization and contact metamorphism. The absence of marker beds and the gradual gradation from one rock type to another,
combined with a scarcity of good exposures makes formational division somewhat arbitrary.

The following is a summary of the stratigraphy which has been described by Ransome and Calkins (1908), Umpleby and Jones (1923), and Shenon and McConnel (1939). The sequence is from oldest to youngest.

1. **Prichard Formation**  The formation is at least 12,000 feet thick, though the base has not been found. It consists of banded, soft, easily eroded slate and argillite, and two quartzitic zones of about 1,000 feet in thickness each. The color is predominately a dark blue-gray to black. It becomes more siliceous and sandy in the upper strata as it grades into the Burke formation.

2. **Burke Formation**  The Burke formation averages about 2,000 feet thick and consists of argillaceous quartzite in the lower parts and more massive buff colored quartzite in the upper parts. The Prichard-Burke contact is fairly definite, but there is a transition zone several hundred feet in thickness where the Burke grades into the overlying Revett formation. Disseminated sericite and siderite are common throughout most of the formation. It forms many of the peaks and outcrops in the district.

3. **Revett quartzite**  This formation is a more massive and pure quartzite than appears in the Burke formation. The Revett reaches a total thickness of 3,400 feet. The middle part is a hard, white quartzite that becomes less pure and more thinly bedded in the upper and lower members as it grades into the underlying and overlying formations. It is the most
resistant formation in the region and is often exposed on the peaks and ridges.

4. **St. Regis Formation** The formation overlies the Revett quartzite and is approximately 1,200 feet thick. It consists of purplish gray and greenish gray quartzites and argillites. Sun cracks and ripple marks are abundant. The rocks do not characteristically form prominent outcrops. Going up the section, the contact between the Revett quartzite and the St. Regis formation is determined by the first appearance of purplish rocks.

5. **Wallace Formation** The thickness of the Wallace formation within the district is judged to be between 4,500 and 6,000 feet. It is distinguished by thin bedding and an abundance of carbonates. The outcrops have a striped appearance due to thin beds of varying composition. The colors are predominantly white, gray, brown and black. The individual beds range from two inches to two feet in thickness and consist of argillite, limestone, sandstone, mudstone, and mixtures of all of these.

   Hydrothermal alteration has produced pale or greenish shades in the Wallace south of the Osburn fault.

6. **Striped Peak Formation** The thickness of the Striped Peak formation is not known, because it has been subjected to erosion, but about 1,500 feet have been observed. The lithology is similar to that of the St. Regis formation, consisting of purplish to pink quartzites and laminated purplish-gray shales.
Quaternary Deposits

The valleys contain sand, silt and gravel transported by streams and valley glaciers. This area was not covered by the ice sheet, so certain problems in geochemical prospecting are thereby not encountered, such as the possible blanketing of the surface with transported materials. Terrace gravels left at past erosion levels at elevations up to 5,800 feet were reported by Ransome.

Igneous Rocks

The igneous rocks of this district consist of intruded monzonite and syenite stocks and lamprophyre and diabase dikes. The Cretaceous intrusives are generally considered to be outliers of the Idaho Batholith, though this has been denied by Anderson.

While the abundance of quartz varies to the extent that the stocks are classed both as monzonite and syenite, they are generally considered to be monzonite. The monzonite consists of nearly equal amounts of plagioclase and alkali feldspars, hornblende, some quartz, and the accessories pyroxene, titanite, magnetite and a little apatite. The outcrops are small in areal extent (see Fig. 2), but their presence provides a theoretical source for ore deposits of the district. Anderson has published several articles discounting the theory that the ores are related to

the Idaho Batholith or the local stocks and claiming that the ores are associated with later Tertiary magmas.

The intruded rocks have caused contact metamorphism of the country rock for distances of 200 to 500 feet from the contact, producing a granitic textured, mica-rich halo. Ore deposits in the contact zones are unimportant.

The dikes in the district seem to be associated with strong faults and mineralization. The dikes are of two types: pre-mineral diabase and post-mineral lamprophyre. The diabase is a greenish brown, medium-grained rock consisting of feldspar embedded in a black, fine-grained groundmass of pyroxene. The lamprophyre dikes are fine to medium-grained, dark gray rocks. They are distinguished from the diabase by an abundance of hornblende and biotite. The dikes weather easily and seldom crop out. Their strike is generally northwest-southeast.

Structural Geology

In the Coeur d'Alene district, the Belt series has been extensively deformed, but the uniformity of the lithology, lack of marker beds, and the scarcity of good exposures have hindered efforts to do extensive detailed mapping.

A few large, pitching folds can be traced for several miles, but minor folds with amplitudes as little as an inch are numerous, as in the Wallace formation. Limbs of the major folds generally dip 45 to 90 degrees. Fracturing and shearing are common to all the rocks, and in
many places good fracture cleavage can be seen. Ripple marks and sun cracks show in many places that the beds have been overturned.

There are several large, high angle faults traversing the district, including the well known Osburn fault whose strike (N 80 W) is closely followed by the South Fork of the Coeur d'Alene River. The most persistent faults lie south of the Osburn fault and strike nearly east-west. The strong faults north of the Osburn fault trend more nearly north-south. The Osburn fault itself has a southerly dip and can be traced for at least 75 miles. The horizontal displacement of the Osburn fault is not known, but Shenon and McConnel state that the vertical displacement may be over 45,000 feet. It has a wide crushed zone and creates saddles where it intersects ridges.

Ore deposits are associated with the smaller faults, those measured in thousands of feet rather than miles and having displacements of a few hundred to one or two thousand feet.

Ore Deposits

The ores of the district are predominantly those of lead, zinc, and silver, with minor amounts of copper, antimony, gold, and tungsten. The deposits are metasomatic replacements and fissure fillings along faults, tensional fractures, and shear zones in quartzite and argillite. The quartzitic rocks belonging to the Burke, Revett, and St. Regis formations are the most favorable for mineralization, and these three formations contain most of the ore in the district; though the Prichard
formation is an important host rock in the Pine Creek and Ninemile areas.

The principal ore minerals are galena, sphalerite, and argentiferous tetrahedrite (freibergite). A total of 105 minerals, including oxides, that are found in the district are listed by Mitcham.\(^1\)

The gangue minerals are quartz, siderite, carbonates, barite, and pyrite. Siderite is the most favorable gangue mineral for ores in the Silver Belt. The ores and gangue minerals vary in different parts of the district, but the differences, as pointed out by Ransome\(^2\) are not so much in types of minerals as in the relative abundance of different ones. The gold and tungsten deposits which occur in quartz veins near Murray are distinctive from the other ores of the district. The other ores may be classified as lead-zinc, lead-silver, and lead-copper-silver ores. Galena and sphalerite are fine-grained, and the two are often found intimately mixed.

According to Sorenson\(^3\), the sequence of mineralization is (1) formation of strong chloritized zones accompanied by magnetite and specularite (2) bleaching and sericitization (3) structural adjustments with deposition of carbonate and quartz, and pyrite or chalcopyrite with or without tetrahedrite (4) reopening of the veins and deposition of silver.

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lead, zinc, and copper with quartz.

The ores often fade gradually into the country rock, making the exact limits of the ore difficult to define. Mineralization is not continuous through the length of the veins, but is sporadic. The problem in prospecting is locating the ore shoots along the vein, once a vein is opened.

The most important developments during recent years in this district have come from the discovery of high grade ore at depths far greater than it was previously suspected to exist\(^1\). The tops of ore shoots may be encountered as much as 3,000 to 4,000 feet below the surface, with little or no surface evidence of their presence. The cost of exploring such ores may be from one to two million dollars.

Hydrothermal Alteration

Considerable attention has been given to hydrothermal alteration which occurs in the Coeur d'Alene district in zones of structural weakness. Mitcham\(^2\) and Sorenson\(^3\) have published descriptions of this alteration. Zones of "bleaching" vary in width up to a mile or more. The zones of alteration appear to show a pronounced enrichment in potash. Abundant sericite is a feature and chlorite is developed to a lesser degree. The altered rocks are a uniform light green shade outward along faults and

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jointing planes. This change in color, due to the destruction of the coloring material, mainly iron oxides and carbonaceous matter, has led to the use of the term "bleaching." The bleached zones appear to be closely associated with faults which served as solution channelways. Sorenson has discussed the use of bleaching as a guide to exploration for ore in the district.

The Star Ore Body

The Star mine is Idaho's leading zinc producer, providing twenty-four percent of the total zinc output.

Mineralization has occurred along a steeply dipping shear zone with considerable gouge and fracturing of the quartzite. In the upper levels the dip averages 80 degrees north, but at greater depths the vein becomes vertical. The main structure strikes north 80 degrees west and cuts the Revett and St. Regis beds nearly at right angles, (see Fig. 7).

The entire length of the lode is 4,000 feet, but the Star-Morning common end line divides the structure nearly equally. In the Star mine, ore exists from near the surface to a known depth of 6500 feet. In longitudinal section the Star-Morning ore body has a tear-drop shape, with the broad end upward.

In the upper levels of the mine the geology is complicated by much vertical and lateral splitting and merging of faults and veins. Mineraliza-

1. Gale, Hoyt S., Geology of the 'Dry Belt' adjacent to Big Creek, Coeur d'Alene Mining District, Idaho; private report, Feb., 1936.
tion occurs in a zone of shears and faulting. The strongest fault is called the Star fault, though in many parts of the mine it is impossible to say which is the Star fault.

The ore is pockety and highly variable in width. Often a wide high-grade vein is actually composed of a multitude of small, closely spaced fissure fillings. The ore grades gradually into the wall rock, so that determining the economic width is a problem to the miners.

In many places the enclosing quartzites are strongly sericitized and display a slaty cleavage. All of the beds dip steeply.

Both acid and basic dikes cut the ore nearly at right angles. The largest dike is about 50 feet in width and nearly vertical. Smaller dikes are numerous, and in places follow the veins. The diabase dikes are pre-mineralization and the lamprophyre dikes post-mineralization.

Many small cross-faults cut the ore, but the displacements create no serious problems.

The ore minerals are sphalerite and galena, with the ratio of zinc to lead being about two to one. A small amount of silver accompanies the galena. The sphalerite and galena are mostly fine-grained and well mixed. The gangue minerals are quartz, siderite, barite, pyrite, calcite, ankerite, and clay. The clays which make up the gouge are the most abundant and quartz the second most abundant gangue minerals.
WEATHERED PRODUCTS

The cycle of weathering is familiar to all geologists. Geochemical prospecting by soil sampling is concerned with the weathered vein products as they exist in sufficient amounts in the soil to serve to indicate a commercial ore deposit. The reader is referred to E. A. Sergeev for an analysis of dispersion and geochemical halos.

Dispersion

The processes by which trace metals derived from a vein become distributed through the soil are very complex, involving the chemical and physical breakdown of the rocks and minerals and the subsequent dispersion of the weathered products. The products of weathering are those approaching stability in the new environment, and consist mainly of the metal oxides, sulfates and carbonates, quartz, and the clay minerals. Fragments of the original minerals will, of course, exist in decreasing size and abundance outward from the source. The exact chemical state of the metals, when part of the soil, is not usually known. They may be ionic, or held in clays so that they are difficult to extract.

A fundamental fact to be kept in mind when prospecting is that the relatively insoluble minerals tend to lag as part of the residual soil, while the more soluble ones are more subject to leaching and become more

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widely dispersed, and are thus necessarily more diluted. The distance
that an appreciable amount of material is distributed throughout the over-
burden depends not only upon the solubility of the mineral, but on the acid
and carbonaceous content of the soil, the amount of rainfall, abundance of
vegetation, thickness of the overburden, slope of the ground and possibly
other factors. When the rainfall is sufficiently great, the mineral salts
may be leached from the upper horizons of the soil faster than they are
formed. In this case soil sampling might not produce any information, or
sampling at a considerable depth might be necessitated.

Opposed to the near surface leaching process is capillary action,
whereby minerals in solution are brought upward through minute passages
in the soil and concentrated in the leaves of plants by absorption and
evaporation. Plants that concentrate unusual amounts of metals in a
direct ratio to the amounts available in the soil are called "accumulator"
plants. The accumulation of vegetal material on the ground produces a
humic layer at the surface that may be abnormally high in metal content.
This process is a manifestation of the Goldschmidt Principle.

In arid regions, mechanical dispersion will predominate over
chemical dispersion. The downhill movement of unconsolidated material
is always present where the ground is not level. This constant downhill
movement is called soil creep, and on steep slopes it is very pronounced.

1. Rankama, Kalevro, Some recent trends in prospecting; biochemical
and geobotanical methods; Mining and Metallurgy, vol. 28, pp 282-284,
1948.
The effects of soil creep must always be considered when interpreting geochemical investigations. It is possible for a halo to be completely buried by soil transported from higher elevations.

The concentration of the indicator metals sought in the soil is mainly a matter of dilution. The strength of a particular anomaly involves a number of variables, such as the size and richness of the ore body, thickness of the overburden, extent of weathering, and the amount of rainfall. However, in geochemical studies, it is the anomaly, or high ratio of the local metal occurrence to the average for the area that is sought, and the exact metal content is not so important.

Halos

The zone containing abnormal quantities of metals derived from an ore body has been designated by Sergeev\(^1\) as the "geochemical dispersion field."

Metal content is highest in the ore body and lowest in the country rock. This spatial relationship is termed by Sergeev as the "train of dispersion." When the sought for trace metals have been deposited in high concentrations in a position so that they cannot be traced to the parent vein, a "false halo" is said to be created.

The size and shape of a halo will depend upon the factors affecting dispersion and, in practice, the sensitivity of the tests employed and the lowest value selected as being significant.

\(^1\) Sergeev, E. A., op. cit., pg. 22.
Halos may be secondary or primary. Minerals formed in place by hydrothermal processes in the country rock enclosing a vein create a primary halo; those which have been transported, as in becoming a part of the soil, form secondary halos.

The various patterns assumed by the resulting halos depend primarily upon the strike of the vein with respect to the topography. A vein striking down slope will create a fan-shaped halo, with the broad side downslope. A vein striking at right angles to the slope will cause a broad sheet-like halo on the downhill side of the vein. When the terrain is flat, the dispersion will be downward, and the halo will widen at depth from the apex of the vein. In the latter case, the halo will be relatively narrow at the surface and the chemical anomaly symmetrical, if plotted graphically. Graphs of chemical anomalies produced by veins cropping out on slopes are asymmetrical, because of the downhill creep of the soil and surface water.

A series of lineated halos could be called a chain. A flat-lying ore body would produce the greatest anomaly where it reached nearest the surface.

The size and shape of the anomalies, and the relative metal values of the anomalies are commonly illustrated on maps by connecting assays of equal values. (see Figs. 9, 10 and 11).

Halos are three dimensional, and cross-sections of the vein, showing the topography with the graphically plotted anomaly, should be
studied to understand the effect of taking samples from different depths in the soil. Figure 1 illustrates how soil samples taken from the lower parts of Sample hole A would be substantially higher than if taken from the upper levels, while just the reverse is true of sample hole B, which is some distance downslope from the outcrop. In the illustration, the halo is divided into zones of different concentrations, increasing from 1 inward to a high of 8 at the vein itself.

Secondary halos may be created at the surface by circulating waters. If fissures exist above a deep ore body, the metals may reach the soil mantle, but if the overlying rock is unfractured, the ascending solutions will be stopped.

Soils

The rate of accumulation of residual materials formed by rock weathering is not known, but it is a very slow process. The rate of rock disintegration will vary greatly with the climate and rock types involved. Usually, several feet of rock are required to form one foot of soil. Water attacks all rocks to a greater or lesser degree, especially when it is charged with carbonic acid. The presence of organic and humic acid also plays a part in accelerating weathering. Weathered pyrite forms hydro-sulphuric acid, a very strong acid which attacks the rocks. The residual materials are mostly silica, clays, metal oxides, carbonates, and sulphates which, when combined with carbonaceous materials, form the soil mantle. A climate which is warm and moist, a deep water table, high
CROSS SECTION OF A HYPOTHETICAL VEIN WITH HALO AND SOIL PROFILE SHOWN
(NUMBERED LINES OUTLINE ZONES OF MINERAL CONCENTRATIONS)

FIG. 1
relief, and a deep penetration of plant roots all promote the rapid decay of rocks. Most of these conditions exist in the Coeur d'Alene district, but there is a wide variance in resistance of different rock types. The Burke and Revett quartzites are very resistant, while the shales, mudstones, and argillites which appear in the Prichard, Wallace and Striped Peak formations are easily eroded. A thick growth of vegetation prevents excessive erosion.

By general practice, the principal soil horizons are defined as A, B, and C. A and B are parts of the solom, or the soil formed by weathering and in which plants grow. The C horizon is the weathered rock material below the solom. Normally, the topmost horizon of the soil has been subjected to the most leaching by rainwater containing humic complexes and organic acids and is therefore relatively low in soluble salts and colloidal material. The clay minerals are carried downward to form the clayey zone, B.

In the areas of flat or nearly flat topography, weathered rock and vein material in the soil may be undisturbed from their original position, so that residual vein material may be continuous with the primary structure. Hawkes and Lakin have defined such structures as "vestigial ore

deposits in residuum. Thus a gently dipping ore body with a thick soil covering may form a vestigial outcrop in the soil and create a geochemical halo at the surface which is at a considerable distance from a position directly above the bedrock ore.

The soil of the Coeur d'Alene district has an upper thin humus layer underlain by a sandy clay. The sandy clay grades downward into coarse angular fragments of bedrock. The soil is residual, immature, loose, unsorted, and does not display distinctive horizons. The thickness varies from zero at outcrops to about 50 feet on gentle slopes.

When prospecting for ore by soil sampling it is important to remember the effect of dilution due to a thick overburden. Generally, ridges have had a much larger proportion of the loose material removed than have the lower slopes. Thus, a uniform vein traversing across ridges, slopes, and valleys would yield relatively high soil assays on ridge tops, moderate ones on the slopes, and possibly none in the valleys where the dilution would be extremely high.

The depth selected for the gathering of soil samples may be unimportant as to net results in some districts, but a particular depth may be desirable in other regions to obtain consistent results or sufficient concentrations of trace metals. Each district will have its own peculiarities of soil profile and geologic conditions which will determine the most suitable sampling horizon.

When deep sampling is required, a soil auger or even powered
drills may be employed.

GEOCHEMICAL INVESTIGATIONS

Field Work

The field work involved in a soil sampling project consists of the systematic gathering of samples and the making of all geological studies that may aid in the location of an ore body.

The area overlying the Star vein was selected for geochemical prospecting because the Star mine workings have made known the structure and extent of the ore, providing a good test area, and because the sampling could be extended so as to explore adjoining ground.

The field work for the Star project was laid out as follows. First, a transit line, Base Line A on the included maps, was run for control westward from the Star-Morning common end line on a bearing nearly parallel to the topographic contours. Sampling lines, which are the lines along which samples were taken, were extended both north and south at right angles to the base line. The sampling lines are lettered on the maps as A-1, A-2, .... The lines labeled Base Line B and Base Line C are control lines run to enlarge the sampling program. The sampling lines were located 400 feet apart along the base lines. Samples were taken at 200-foot intervals along each of the sampling lines. Thus the reconnaissance spacing intervals were 400 feet parallel to the strike of the vein and 200 feet at right angles to the strike. In consideration of the
size of the known veins of the general area and the probable dispersion of
the trace metals, this spacing was calculated to be adequate to detect any
mineralization of consequence.

When a significant anomaly was found outside the halo of the main
Star vein, that locality was resampled on a 50-foot grid to define its
limits and to check against possible contamination of the original samples.

The field work was done by two men, using a tape and Brunton
compass. A helper carried the front of the tape and cut brush, while the
geologist kept him on line and plotted the line and sample locations on field
maps. The measured slope distances were converted to horizontal dis­
tances. The Brunton survey work was kept within one per cent limit of
error. In purely exploration reconnaissance work, such accuracy would
not be necessary, at least not until an anomalous area was encountered.
Sample locations could be made by spotting positions on aerial photos or
by pacing distances along compass bearings. In the Star project, con­
siderable accuracy was required in order to correlate the results with
the known structures.

A scale of 200 feet to the inch was used for field mapping. Surface
geology was mapped simultaneously with the sampling. Since there are
relatively few bedrock exposures in this area, the surface geologic map­
ing consisted mainly in describing the float.

Survey stations were marked by blazing trees or driving lath and
attaching metal tags. The exact sample location was not marked on the
ground, but it was plotted on the field maps and could easily be relocated by taping from the nearest station.

The actual sampling consisted of scraping aside the leaves and grass at the surface and digging up about a cupful of soil. An ordinary garden trowel was used for this and was easy to carry. The soil was then screened through a 10 by 10-inch 2-mm mesh wire screen. The screened soil was caught on a sheet of waterproof paper and poured into a manila envelope having a metal tab to hold it closed. The envelopes should have waterproof glue, because the soil is moist. The envelope was labeled to indicate the sample location by noting the number of the sample line and the number of the sample as taken along that line.

Each day the sampling crew left the samples at the assay office on the return trip from the field. The number of samples taken daily varied from 10 to 55, depending upon the amount of brush encountered, time required to reach the working place, and the weather.

The writer found that samples taken from the topmost layer of soil over the Star ore body gave results which showed a true relation to the underground geology, and proved satisfactory for prospecting in this area.

Soil samples were taken at 6-inch intervals to a 6-foot depth in an effort to determine the effect of sampling at depth. There was some indication that the assays ran highest at depths or two to four feet below the surface, but not enough of this testing was done to yield any definite results.
Although no difficulty was encountered from contamination of the samples in the field, a few precautions must be observed. These include using tools or equipment from which paint, solder or galvanized coating could not be rubbed into the sample, avoiding the wearing of clothing which may contain mineral dust from mines, mills, or smelters; and particular attention should be paid to eliminate areas which may be contaminated by dumps, mill tailings or smelter dust.

The total area covered by sampling in this project was approximately one and one-half square miles. A total of 792 samples was taken, and 1,292 analyses were made on the samples.

Laboratory Methods

The required speed, economy, sensitivity, and accuracy of sample analysis may be achieved by either spectroscopic or colorimetric methods. Due to the expense of suitable spectroscopes, their lack of portability and the necessity of having a highly skilled operator, these instruments are not employed for this type of work in America. Russia and Sweden, however, have made extensive use of them in geochemical work.\(^1\)

Two distinct types of colorimetric methods have been devised. In the first, the heavy metals are extracted in solution and an organic

---

reagent is used to measure the quantity, in what is basically a titration method. The other is a spot test in which a colored precipitate is confined to a spot of controlled area, and the intensity of the color is a measure of the quantity of metal in the sample. For further information on the above methods see the bibliography at the end of this paper.

The first colorimetric method mentioned is employed for the determination of lead, zinc, molybdenum, tungsten, and the heavy metals group. The second, the spot test, is used in the determination of copper, nickel, cobalt, and silver.

Three separate tests were employed in the Star project; the lead test, the zinc test, and the test for the heavy metals group. Discussion of laboratory work will be restricted to these three tests.

The lead, zinc, and heavy metals tests rely upon an ultra-sensitive reagent called diphenylthiocarbazone (C₆H₅NHNHNHC₆H₅), commonly called dithizone. Sandell¹ and Welchér² have written comprehensive discussions on dithizone. This reagent is a violet-black solid especially soluble in chloroform and carbontetrachloride to form a green solution. When a carbontetrachloride-dithizone solution is mixed with an aqueous solution containing a heavy metal, the dithizone is ionized and a

hydrogen ion is replaced by one of the heavy metal ions, forming a complex dithizone. The metal dithizone gives the solution a distinctive color which is dependent upon the particular metal, or group of metals present, and the quantity.

The following 17 metals react with dithizone to form dithizonates: manganese, iron, cobalt, nickel, copper, zinc, lead, silver, cadmium, indium, tin, platinum, gold, mercury, tantalum, palladium, and bismuth. However, only the tests for lead, zinc and copper employ dithizone, as other tests exist for the other metals. Tests can be made for a single metal or for a selected group of metals by adjusting the pH or adding a reagent to form complexes of the interfering elements, or both.

Determinations made by using dithizone may be by the mono-color method or by the mixed color method. In the mono-color method, successive aliquots of a carbon tetrachloride-dithizone solution are added to an aqueous solution of the proper pH for the particular test until some of the original green color remains, indicating that all the metal has been extracted. The sample solution is then shaken with a buffer solution to remove the excess dithizone. The color must match that of a standard solution prepared under identical conditions, and the intensity of the color indicates the amount of metal present. The mono-color method is less satisfactory and convenient than the mixed color method. In the mixed

color method the excess dithizone remains unreacted. Measured portions
of the dithizone solution are added to the sample solution until a mixed
color is obtained. The hue indicates the amount of metal present. The
color series is green, blue-green, blue, purple, purplish-red, red. The
test is most accurate in the red-purplish and purplish range. In both
methods the colors are compared with tables which indicate the amount
of metal present for a given color of the sample-dithizone solution.

Dithizone is so sensitive that two-thousandth of one part in a
million of metal can be detected. But in soil sampling work, where the
assaying of a large number of samples rapidly and cheaply is necessary,
al possible short cuts are taken; and a 30 per cent limit of error is
considered sufficiently accurate by the U.S. Geological Survey. In most
cases, a 100 per cent limit of error would allow the detection of an anom-
aly.

The outstanding feature of the tests used is the requirement of
absolute cleanliness of the reagents and all equipment. If one so much
as touches with his finger any equipment which comes into contact with
the sample, the assay will show excessive values as a result of contam-
ination.

A room in the idle Hecla mill at Gem, Idaho was converted into a
laboratory for making the soil analysis. The Hecla Mining Company
assayers had no special training for this radically different type of work,
but they achieved excellent results as regards both consistancy and
When samples were received at the laboratory, they were first dried, then mixed by rolling on waxed paper and then screened through an 80-mesh stainless steel screen. A laboratory balance was used to weigh out 0.33 gram samples for analysis. All metals were first analyzed for heavy metal content. The heavy metals test is a composite test for lead, zinc, and copper. After all the heavy metal tests were completed, those samples found to be abnormally high in metal content were analyzed by the lead and zinc methods. The heavy metals test was the principal test employed because it gives a combined result for the commercial minerals of the area, and because of the reported successful use of this test at the Reeves MacDonald Mine, Ltd., in British Columbia. The lead and zinc tests were performed to check the heavy metals test, to determine the relative values of the different tests in this district, and to localize the anomaly.

Due to the pH adjustment (6.2) in the heavy metals test, twice the weight of copper and four times the weight of lead are required to yield the same result as an equal amount of zinc. Thus the heavy metals test is most sensitive for zinc, less so for copper, and still less for lead. The results are expressed as zinc equivalents. The parts per million of heavy metals as determined by the test, theoretically, would be

\[
\text{Zn equivalent (in ppm)} = Zn + \frac{Cu}{2} + \frac{Pb}{4}
\]
The procedures employed in the analysis and the Hecla modifications are given in the appendix. The procedures listed are those compiled by Lakin, Almond, and Ward.

Results

Sampling showed background counts of approximately 60 ppm for heavy metals, 50 for zinc and 30 for lead. The ratio between the highest assay encountered, 12,000 ppm, and the background, taken as 60 ppm, would thus be 200 to 1. Ratios of 10 or 12 to 1 were common for the halo over the Star vein.

Early results indicated a satisfactory increase in values as the position of the vein was crossed, and an expected gradual decrease on the downhill side due to the down slope movement of the soil.

The included plan maps showing the geology and topography, and the heavy metals, zinc and lead assays are constructed so that they can be superimposed. When placed together on a light well, the maps reveal the relationships of the ore structures and topography to soil sampling results.

An interpretation of the results will be made by discussing the most outstanding features of each of the assay maps and cross-sections.

Soil Assay Maps

The heavy metals assay map (see Fig. 9) shows the heavy metal

assays and the halo produced by outlining the results at 90 ppm and over. Some of the outlying shaded areas which are not significant could have been eliminated by outlining on the basis of 100 or 110 ppm.

The long dimension of the halo parallels the strike of the Star vein. The lobe protruding from the western end marks the extension of a strong fault which crosses the area. The branching fissures to the west create a wide irregular section of the halo.

For purposes of illustration, it is regretted that sampling could not have been done over the Morning portion of the vein, so as to reveal the entire shape and extent of the halo.

The relative high solubility of zinc compared to lead is illustrated by the broader and less pronounced halos revealed by the heavy metals and zinc tests. A comparison of the tests and their anomalies is best shown by the included cross-sections (see Figs. 3, 4, 5 and 6).

It can be seen that the highest assays, apparently displaced, appear along sampling lines B-1 through B-6, where the assays are as high as 12,000 ppm. The topographic map of the area (see Fig. 7) suggests that the highest assays were due to contamination of the soil from the area over the best ore, which is uphill from the high assays. However, a low ridge between the two gullies which diverge from the Star 1200 portal would divert such material down the gully to the east. The anomaly is neither high nor extended along this east gully.

Since sampling results depend upon the degree of dilution of the
trace metals, a careful study of the surface conditions is required for the interpretation of the results. Field observation disclosed that directly over the central portion of the Star vein the overburden was quite thick, probably about 30 feet, while in the vicinity of the exceptional assays there was a very thin covering of soil and outcroppings of bedrock. Even though ore presumably is not present along this part of the vein, this lack of dilution, combined with a mere trace of metal can produce very anomalous effects at the surface. It is possible that the west end of the ore rakes at a steep enough angle so that good ore actually is present at this part of the vein above the highest underground workings. As yet no work has been done to prove or disprove this possibility.

The group of samples located along line B-16 at 50-foot intervals are check samples taken because of reported high assays from line B-16. The check samples were all, except for the few scattered shaded ones, below the significant count. A check of the laboratory work indicated that the original high assays were due to contamination of the water used in the analysis by a rubber hose through which it was being siphoned.

An extraordinary assay near the southern end of line A-1 marks an abundance of manganese and iron oxides exposed in weathered vein material exposed by a road cut at that point. The oxidized material is about six feet in width and is probably associated with the We Like vein. The narrowness of the effects of the above material is surprising, but dilution at this point is high because of the thickness of the soil. One
assay taken directly from the exposure assayed 11,000 ppm; but eight samples taken within a 100 foot radius were all 750 ppm or less (see also Table I).

The zinc assays are also outlined at 90 ppm and over (see Fig. 10). The outlines are quite similar to those for the heavy metals. The three outlying shaded spots are present on all maps and they appear to correlate with mineralization encountered in diamond drill holes. (see also Table II).

The lead halo is outlined at 90 ppm (see Fig. 11). Examination of the assays shows more abrupt rises between the background and the anomalous area. The width of the halo is more restricted at the eastern and western extremities because of the greater specific gravity of lead and its greater insolubility and the resulting more limited downhill dispersion. (see also Table III).

Cross-Sections

Four cross-sections of the veins as revealed by underground workings have been prepared. Their positions are indicated on each of the plan maps. The assays for the three tests are indicated graphically on each section.

Section A-A' is 3,200 feet long and is near the Star-Morning end line. (see Fig. 3) It can be seen that the lead anomaly is more restricted to an area directly over the vein than those of the heavy metals and zinc, again illustrating the relative insolubility of lead. Each of the metal
assays shows three peaks corresponding to the three known veins. The lead assays appear to indicate more of the known relative richness of the veins than the others do. The highest assays are about 450 ppm for lead and heavy metals and 300 for zinc.

Section B-B' is located 800 feet west of the end line, (see Fig. 4) where two important veins are known to exist in the upper levels. The graphs of the assays show two corresponding highs.

Lead gave by far the highest assays, 400 ppm, while the heavy metals gave up to 275 ppm and form almost identical curves.

The typical downhill shift of the anomalies resulting from soil creep is evident in each section.

Section C-C' is 1600 feet west of the Star-Morning end line, and its length is 5,600 feet, (see Fig. 5) The section crosses the locality where the highest values were encountered. This spot is represented by the very conspicuous rises in the lead and heavy metal curves.

The lead and heavy metals are between 800 and 900 ppm, whereas the zinc anomaly is low and broad, the highest values being 200 ppm. Four veins are crossed, and four peaks exist on each of the assay curves, though they are rather obscure on the zinc curve. The vein cropping out on the steepest part of the slope also shows the greatest amount of downhill migration.

Section D-D' is still farther to the west than the others, (see Fig. 6) and beyond the limits of any known commercial ore. The numerous
fissures in this area and closer sampling spacing give rise to more complicated graphs. The section also crosses the area of most intense soil enrichment, where the highest assays are found. The zinc, while generally quite low, tends to level out the somewhat erratic lead and heavy metal curves, and indicates more clearly the separate veins.
<table>
<thead>
<tr>
<th>Parts per million of heavy metals</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 90</td>
<td>627</td>
</tr>
<tr>
<td>90-150</td>
<td>71</td>
</tr>
<tr>
<td>151-200</td>
<td>31</td>
</tr>
<tr>
<td>201-250</td>
<td>10</td>
</tr>
<tr>
<td>251-300</td>
<td>14</td>
</tr>
<tr>
<td>301-350</td>
<td>5</td>
</tr>
<tr>
<td>351-400</td>
<td>11</td>
</tr>
<tr>
<td>401-450</td>
<td>3</td>
</tr>
<tr>
<td>451-500</td>
<td>5</td>
</tr>
<tr>
<td>501-550</td>
<td>1</td>
</tr>
<tr>
<td>551-600</td>
<td>0</td>
</tr>
<tr>
<td>601-700</td>
<td>0</td>
</tr>
<tr>
<td>701-800</td>
<td>7</td>
</tr>
<tr>
<td>801-900</td>
<td>2</td>
</tr>
<tr>
<td>901-1000</td>
<td>1</td>
</tr>
<tr>
<td>*1000 and over</td>
<td>4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>792</strong></td>
</tr>
</tbody>
</table>

The total number of samples taken is 792. Of these 164, or 20.7 per cent were 90 parts per million of heavy metals or over; assays under 90 parts per million were considered background counts. Of the 164 assays which were 90 or more ppm, 102, or 62 per cent, were between 90 and 200 ppm.

*The highest assay encountered was 12,000 ppm of heavy metals (1.2%).
Table II

TABULATION OF ZINC ASSAYS

Only part of the samples were analyzed for zinc content. The samples analyzed for zinc were mostly from the anomalous area.

<table>
<thead>
<tr>
<th>Parts per million of zinc</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 90</td>
<td>45</td>
</tr>
<tr>
<td>90-150</td>
<td>74</td>
</tr>
<tr>
<td>151-200</td>
<td>42</td>
</tr>
<tr>
<td>201-250</td>
<td>3</td>
</tr>
<tr>
<td>251-300</td>
<td>3</td>
</tr>
<tr>
<td>301-400</td>
<td>3</td>
</tr>
<tr>
<td>over 400</td>
<td>0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>170</strong></td>
</tr>
</tbody>
</table>
Table III

TABULATION OF LEAD ASSAYS

Only the samples which were analyzed for zinc were analyzed for lead.

<table>
<thead>
<tr>
<th>Parts per million of lead</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 90</td>
<td>62</td>
</tr>
<tr>
<td>90-150</td>
<td>17</td>
</tr>
<tr>
<td>151-200</td>
<td>11</td>
</tr>
<tr>
<td>201-250</td>
<td>9</td>
</tr>
<tr>
<td>251-300</td>
<td>11</td>
</tr>
<tr>
<td>301-400</td>
<td>17</td>
</tr>
<tr>
<td>401-500</td>
<td>11</td>
</tr>
<tr>
<td>501-600</td>
<td>12</td>
</tr>
<tr>
<td>over 600</td>
<td>18</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>168</strong></td>
</tr>
</tbody>
</table>
COSTS

The costs of exploration programs are important to practical mining men.

All laboratory equipment and reagents were obtained from Denver Fire Clay. The equipment, including the Barnsted demineralizer but excluding the laboratory balance, cost $703.00 but not all of it was used. The reagents cost $254.00. A considerable saving was made by purchasing technical grade carbon tetrachloride and distilling it. Technical grade carbon tetrachloride costs only one-fourth as much as reagent grade.

Once the initial investment is made to equip a laboratory, the expense of continuing the work is essentially the wages of the men employed. One man can do the laboratory work and analyze from 30 to 60 samples a day. Two men will normally be employed in the field, though it is possible for one man to do sampling if only approximate location of the samples is required, as when spotting sample locations on aerial photos. Of course, any number of crews might be engaged in the work, depending upon the scale of the project and desired rate of progress.

In a region of flat topography and in the absence of brush, the field work would proceed much faster than it did in the Star project. If no transit lines were desired, the cost and time involved would be cut drastically.
Field kits for making determinations are available or can be assembled at low cost.

Because the Star soil sampling was primarily a test project and new to all the members engaged in it, the total costs to the company have no significance to others.

CONCLUSIONS

It may be concluded that the value of soil sampling was proved by this project in that the Star ore body could have been discovered by this method. Soil sampling is especially valuable to districts where there is a blanket of soil concealing the bedrock, where little surface evidence of veins exists, and when the costs of other exploration methods are high.

A comparison of the lead, zinc, and heavy metals tests in this area showed that the heavy metals test gave better results than did the zinc. While the heavy metals test is convenient for reconnaissance work, the lead test yields a much sharper and more pronounced anomaly and serves to more or less pinpoint the ore structure. It might be advisable to use the lead test in conjunction with the heavy metals test when prospecting.

While this work was confined to the above three tests, procedures are available for copper, cobalt, molybdenum, silver, tungsten, and nickel. Experimental work is being conducted to develop suitable tests for other metals. Due to the abundance of copper and silver in the Silver Belt of the Coeur d'Alene district, the copper and silver test could be
employed here. The U.S. Geological Survey Circular 161 gives a procedure for obtaining the silver, lead, and zinc values on the same sample. This test should be suitable for this district.

The Star vein produced an anomaly that was graphically almost ideal because of the nearness of the ore to the surface and the large size of the deposit. The results are no doubt better defined than they ordinarily would be. It may be assumed that a blind ore body at great depth with the absence of ascending solutions could not be detected by surface sampling. The extent to which soil sampling can be effective over deep seated veins is a field for further study.

Geochemical investigations should be preceded by geological study to determine structural trends, types of ores sought, and expected size, strike, and depth of possible ore deposits.

While soil sampling does not reveal the grade of detected ore bodies, experience and familiarity with the district may enable the prospector to estimate values roughly by comparison.

While geochemical prospecting has proved it has an important place in aiding in making new discoveries, much research is needed in all phases; analytical procedures, geochemical principles and processes, and in interpreting results obtained under widely varied conditions.

Interesting and possibly profitable test projects which suggest themselves are soil sampling over deep ore shoots which carry ore at

depths of 1,000 feet to 3,000 feet below the surface, and the comparing of sampling of bleached and unbleached areas in the Coeur d'Alene district.

It should be understood that geochemical prospecting does not replace other prospecting methods, but is to be used in conjunction with all the tools available to the geologist.
A. View of laboratory in which the Star soil analyses were made.

B. View of laboratory. Barnsted Bantam Demineralizer mounted in corner.
A. Part of laboratory. The shelf holds the graduated cylinders in front of the fluorescent light while estimation of the metal content is made. Test tube digestion rack and hot plate in center foreground.

B. Part of laboratory. Automatic burette with light-proof bottle for dithizone solution in foreground.
APPENDIX

The following procedures are quoted from U.S. Geological Survey Circular 161. The material in the circular was first published as a preliminary report in 1951. Any modifications introduced by the Hecla assayer are described as such. Some facts related to the laboratory work and worthy of special attention are added by the author under Special Notes on Laboratory Work at the end of the paper.

Determination of Heavy Metals in Soil or Sediment

Huff (1951) has described this procedure, and has discussed the reactions involved in the method as well as its usefulness in geochemical prospecting. The test is designed to detect as little as 50 ppm. and as much as 10,000 ppm of heavy metals expressed as zinc equivalents. The test is most sensitive for zinc and least sensitive for lead. Four methods of preparing the sample are described in order of increasing rigor of attack on the sample. If representative samples are treated by all four digestion methods, the digestion method best suited for a particular study can be selected; in general, it will be the quickest method which gives satisfactory results. The test is easy to make and only simple apparatus and reagent-grade chemicals are required to make 60-80 tests per man day in a make-shift laboratory. The test has been used in reconnaissance studies.

Reagents and apparatus

Dithizone (diphenylthiocarbazone), 0.016 per cent weight per volume. Dissolve 0.008 g of dithizone in 500 ml of reagent-grade carbon tetrachloride. Since sunlight and heat decompose the reagent, solutions should be stored in paper-wrapped, glass-stoppered, pyrex bottles and kept cool.

Dithizone, 0.0016 per cent weight per volume. Dilute 10 ml of 0.016 per cent dithizone solution to 100 ml with reagent-grade carbon tetrachloride. When working at temperatures over 70 F, prepare a fresh solution every 4 hr.

Water Pass tap water through resin demineralizer. See "Special Apparatus".

Concentrated nitric acid, approximately 69 per cent (constant boiling). Purify by distilling in an all-pyrex still.

Dilute nitric acid, 1:7.

Hydrofluoric acid, approximately 48 per cent. A.C.S, analyzed grade.

Sodium acetate, 25 per cent. Dissolve 250 g of anhydrous sodium acetate, or 415 g of NaC_{2}H_{3}O_{2}, 3H_{2}O, in water; and purify by shaking in a large separatory funnel with dithizone stock solution. Remove traces of dithizone by shaking with pure carbon tetrachloride. Dilute
Ammonium fluoride, 10 per cent. Prepare by dissolving 100 g of ammonium fluoride in water; purify as with sodium acetate, and dilute to 1.0 liter. Keep in pyrex bottle.

Buffer solution, containing 5 per cent sodium acetate and 1 per cent ammonium fluoride. Prepare as needed by diluting 200 ml of 25 per cent sodium acetate solution and 100 ml of 10 per cent ammonium fluoride solution to 1.0 liter.

Standard zinc solution, 0.01 per cent in approximately 0.1 N hydrochloric acid. Dissolve reagent-grade zinc in a slight excess of hydrochloric acid and dilute to volume. Before use, dilute with pure water and a little additional acid to a 0.001 per cent solution (10 micrograms of zinc per ml).

Huff antibump tubes. See "Special Apparatus."

Digestion tube rack. The digestion tubes can be held conveniently in a wooden frame having a series of 13-mm holes spaced with centers about an inch apart.

1 pipette, 0.1 ml, graduated in hundredths of a ml.

Lucite spoon, a lucite bar with a cavity of 0.25 ml, 7 mm diameter, 6.5 mm deep, drilled near one end.

1 graduated cylinder, 100 ml, glass-stoppered, pyrex.

1 beaker, 250 ml.

3 graduated cylinders, 5 ml, pyrex.

1 separatory funnel, 125 ml.

1 serological pipette, 10 ml, graduated in tenths of a ml.

1 alcohol lamp, small.

1 hot plate, electrical, 110 volt a-c, variable temperature control heating surface 6 by 6 in.

12 platinum dishes, flat-bottomed, without rim, about 20 mm in diameter and 10 mm high.
1 platinum wire, 75 mm long.

1 polyethylene wash bottle, 250 ml.

Colorimetric tubes, 25 by 200 mm glass culture tubes, with screw cap. Mark the tubes with a stylus at volumes of 5, 10, 20, and 40 ml. Glass-stoppered, graduated pyrex cylinders are a satisfactory substitute for the colorimetric tubes.

Procedure

Digestion: Four different digestion methods are described below which represent four distinct steps of increasing rigor of digestion. By the use of all four digestion methods on representative samples the digestion method best suited for use for a particular study can be selected; in general, the best method will be the quickest method that gives satisfactory results. Instructions for the digestions are as follows:

A. Place a scoopful of the ground sample in an antibump tube, add 4 ml of dilute nitric acid and heat over an alcohol lamp. Maintain at or near the boiling point for 10 min.

B. Place a scoopful of the ground sample in an antibump tube, add 4.0 of dilute nitric acid and boil slowly and continuously on a hot plate for 1 hr. Dilute with water to 4.0 ml and mix by shaking.

C. Place a scoopful of the ground sample in an antibump tube, add 1 ml concentrated nitric acid and heat on a hot plate (low heat) overnight without boiling; heat further the following morning (high heat) until about one-half the acid is boiled away. Dilute to 4.0 ml and mix by shaking.

D. Place a scoopful of sample in a 5 ml platinum dish, add 2 ml hydrofluoric acid and 2 ml concentrated nitric acid, mix with a platinum rod. Heat on a hot plate at about 35 °C to 40°C until dry. Cool and add 2 to 5 drops of concentrated nitric acid, heat to dryness again. Add 10 drops of concentrated nitric acid and 10 drops of water and heat. Wash the contents into a tube with water and dilute to 4 ml.

Each of the four digestion methods leaves the sample dissolved in nitric acid of about the same concentration. When the sample solution cools, the solid residue settles to the bottom of the digestion tube, leaving a clear yellowish solution. Aliquots of this are pipetted for the estimation.
Estimation: Place 5.0 ml of the dilute dithizone solution in a clean colorimetric tube, add 35 ml of the buffer solution, 0.2 of the sample solution, and shake for 30 sec. Compare the color of the carbon tetrachloride layer with the color of similar layers prepared by using zinc standards or with the colors listed in table 3 to determine the metal content of the sample (expressed as zinc equivalents, that is, zinc plus one-half copper plus one-fourth lead). If the carbon tetrachloride layer is red or nearly red, clean the tube, using distilled water and dithizone solution. Repeat the determination using a smaller aliquot of the sample solution, to obtain a mixed color (red metal dithizonate plus unreacted green dithizone), so that the concentration can be read from table 4. The color differences are most sensitive near the purplish, midpoint of the range, and this range should be used for greatest accuracy.

Do not use more than 0.2 ml of the sample solution for the determination. The procedure is designed so that samples containing 50 or 100 ppm total heavy metal, a normal background concentration, will give a slight positive test and any concentrations higher than this background will be easily distinguishable. The test, as described, is not suitable for determining heavy-metal contents in the range below 50 to 100 ppm, the normal background range. It is advisable to make many repeat determinations and to run blanks on the reagents frequently to avoid error by contamination. If any check determinations are to be omitted, omit those for 'background' samples.

The principal modification made on the above determination at the Gem assay office was that after digestion by method B the sample solution was diluted to 16 ml instead of 4 ml, so that aliquots four times as large as those given in Table 4 of U. S. Geological Survey Circular 161 could be used, and micropipetting avoided. This proved more convenient and made estimation of the color of the dithizone solutions easier. The use of a laboratory balance rather than a measuring scoop for measuring samples of the soil was more time consuming, but not excessive and it seems likely that this method would be more accurate.

The table on page 62, "Table 4, Descriptive chart of color of dithi-
zone solution for determination of heavy metals, expressed as zinc equivalents according to Huff was not used. Instead, the one given on page 63, prepared by Kennedy, was substituted. This was done primarily because at the outset the sample solution was diluted to 15 ml for a 0.30 gm soil sample. Later, it was found more convenient to use a 0.32 gram sample and dilute the digested sample solution to 16 ml.

The formula used in the construction of this chart is

\[
\frac{\text{micrograms of zinc found in the soil solution}}{\text{grams of soil analyzed}} \times \frac{\text{total ml of soil solution}}{\text{ml of soil solution in aliquot}} = \text{parts per million}
\]

Example: (compare with table on page 63)

\[
\frac{1.5 \text{ (micrograms found in 0.75 ml aliquot)}}{0.30 \text{ gm}} \times \frac{15 \text{ ml}}{0.75 \text{ ml}} = 100 \text{ ppm}
\]

Determination of Zinc in Soils

The field method for zinc in soils and rocks given below is described more fully by Lakin, Stevens, and Almond (1949). In the authors' experience, about 85 per cent of the values obtained by the field method are within plus or minus 40 per cent of those obtained by careful laboratory analysis. The method, as described, is applicable to samples containing 50 to 1000 ppm of zinc. Under the conditions of the test, the reaction of copper with dithizone is largely prevented. However, if the copper content of a sample is ten times that of zinc, the zinc value may be as much as 75 per cent greater than its true value. Care must be exercised to avoid contamination, since erratic results are often due to zinc contamination of the test tubes, pipettes, or reagent solutions. Under favorable conditions up to 60 determinations per man day can be made. The apparatus is simple and portable. The chemicals required for the test are readily available and, except for carbon tetrachloride, are not hazardous. The method has been used widely in geochemical prospecting.

Reagents and apparatus

Potassium bisulfate. Analytical grade ground to fine powder in a

l. Kennedy, V., from unpublished data.
porcelain mortar.

Water. Pass tap water through a resin demineralizer. See "Special Apparatus."

Sodium acetate, 2N. Dissolve 164 g CH₃COONa and dilute to 1 liter with metal-free water.

Acetic acid, 2N. Dilute 114 ml of glacial acetic acid to 1 liter with metal-free water.

Acetate buffer. Mix 5 volumes of 2N sodium acetate with 2 volumes of 2N acetic acid, and remove reacting heavy metals by shaking with 0.01 per cent dithizone solution.

Dithizone solution, 0.01 per cent weight per volume. Dissolve 0.01 g in 100 ml of reagent-grade carbon tetrachloride. Store in cool, dark place.

Dithizone solution, 0.0025 per cent weight per volume. Dilute 25 ml of 0.01 per cent solution to 100 ml with reagent-grade carbon tetrachloride.

Sodium Thiosulfate. Dissolve 50 g of Na₂S₂O₃·5H₂O in 100 ml of water. Remove reacting heavy metals by shaking with 0.01 per cent dithizone solution.

Standard zinc solution, 0.01 per cent in about 0.1 N hydrochloric acid. Dissolve 0.1 g reagent-grade 30 mesh zinc in concentrated hydrochloric acid and dilute to 1 liter. One ml of this solution contains 100 micrograms of zinc. Prepare dilute solution containing 20 micrograms per ml from the standard solution.

20 pyrex culture tubes, 18 by 150 mm, marked at 3, 10, and 11 ml.

20 pyrex culture tubes, 16 by 150 mm, marked at 5 ml.

1 serological pipette, 5 ml, fitted with stopcock at upper end.

1 graduated cylinder, 100 ml, or other suitable device in which to support pipette.

Lucite spoon, a lucite bar with cavity of 0.05 ml, 4 mm diameter, 4 mm deep, drilled near one end.
Lucite spoon, a lucite bar with cavity of 0.25 ml, 7 mm diameter, 6.5 mm deep drilled in one end.

Mullite mortar and pestle, outside diameter of mortar, 75 mm.

2 sieves, 2 mm mesh iron screen and 100 mesh cloth, see 'Special Apparatus.'

1 camel's-hair brush, length of brush part, 18 mm.

1 small spatula, zinc free, length of blade, 50 mm.

1 digestion and fusion rack.

1 gasoline stove.

Procedure

Preparation of Sample Solution. - Fill a lucite spoon, capacity of 0.05 ml, with soil by tightly pressing the prepared soil into the spoon with a small flexible spatula. Wipe the outside of the spoon level with the spatula and tap into a pyrex (18 by 150 mm) culture tube. Add one spoonful (0.25 ml) of powdered potassium bisulfate to the soil sample and place in the digestion and fusion rack. Place the rack with seven test tubes containing soils and one reagent blank on the gasoline stove and heat for about 10 min. or until the soil is essentially decomposed. If necessary, add a little more potassium bisulfate to effect the desired fusion. Remove, allow to cool, add 3 ml of water to each sample, and heat again until a milky suspension is obtained. Prolonged or too violent heating will cause excessive bumping and should be avoided. Add 7 ml of the acetate buffer solution and 1 ml of the sodium thiosulfate solution to each sample, stopper with a clean cork, shake thoroughly, and set aside to allow the suspension to settle and the solution to cool.

Estimation. - This step is essentially a titration. Place 5 ml of the 0.0025 per cent dithizone solution in a pyrex culture tube (16 by 150 mm). Add measured volumes (1.0, 1.5, 2.0, 3.0, and 8.0 ml) of the solution prepared from a soil sample to the dithizone solution and shake vigorously for 1 min., between each addition, using a clean cork to close the test tube. Sufficient sample solution has been added when the color of the carbon tetrachloride layer matches a standard containing 5 micrograms of zinc, prepared as follows: Add 20 micrograms of zinc to the reagent blank carried through the fusion process, dissolve and buffer as above, and shake one-fourth of the solution with 5 ml of 0.0025 per cent dithizone solution. Make new color standard every 30 min. because
The color fades rapidly.

The added increments of the sample solution correspond to zinc content of the soil samples as follows:

<table>
<thead>
<tr>
<th>Milliliter of sample solution required to match standard</th>
<th>Probable zinc content (ppm)</th>
<th>Reported group value (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0------------ 1000 and up</td>
<td>1000+</td>
<td></td>
</tr>
<tr>
<td>1.5------------ 700-1000</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>2.0------------ 400-700</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>3.0 to 8.0------ 100-400</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>excess of 8.0 ml---- under 100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The procedure calls for fusion of the sample with potassium bisulfate. This was tried in the Star project, and about eight per cent extraction was obtained. However, extraction by nitric acid, as in the heavy metals procedure, was more convenient and was used. Extraction by nitric acid was not as complete, but the percentage was a constant and provided results that served as well to show the anomaly. Kennedy[^1] stated that a 1 to 1 nitric acid solution provides a more complete extraction than does the 1 to 7 nitric acid called for in the procedure quoted for heavy metals.

Table IV used for the estimation of the heavy metal assays was also used for the zinc determination.

**Determination of Lead in Soils and Rocks**

The procedure for the determination of traces of lead in soils is based on the method used by Almond and Morris (1951). A nitric acid digestion has been found to dissolve lead more completely than the

[^1]: Kennedy, Vance, oral communication, Aug., 1952.
extraction used by Almond and Morris and is recommended here. A 0.1 g sample is suitable for determination of lead in samples ranging from 10 to 1000 ppm. The lead estimation is made with dithizone in the presence of cyanide as a complexing agent for other reacting metals. The oxidation product formed when an aqueous solution is shaken with dithizone in the presence of citrate, iron (III) and cyanide is a major source of error, but this is avoided in part by diluting the aliquot and by using freshly prepared dithizone. Duplicate samples can be determined to within 20 per cent and generally the value reported differs from a careful laboratory determination by less than 50 per cent. About 35 samples can be determined per man day. The method has been used in geochemical prospecting.

Reagents and Apparatus

**Potassium cyanide, 10 per cent.** Dissolve 50 g KCN in 75 ml water and shake successively with small portions of 0.01 per cent dithizone solution until the final carbon tetrachloride layer is green. Extract the excess dithizone dissolved in the aqueous layer with successive portions of chloroform and discard the chloroform. The final extraction should be colorless. Dilute the solution to 500 ml with metal-free water.

**Potassium cyanide, 0.1 per cent.** Add 50 ml metal-free water to 100 ml graduated cylinder, add about 1 ml of the 10 per cent potassium cyanide solution to cylinder and make the volume up to 100 ml with water. Insert stopper and shake. Caution: Potassium cyanide is exceedingly poisonous; a very small amount taken internally is fatal. Therefore, never transfer a potassium cyanide solution with a pipette; always wash hands immediately after handling the reagent and its solutions.

**Acidification of cyanide solutions produces a lethal gas (HCN).** Never store near acids. Exercise meticulous care to avoid any possible contact of the salt or its solution with acids resulting from breakage in transport. Never acidify solutions containing cyanide. Always wash thoroughly vessels in which the reagent has been used.

**Ammonium citrate solution, 10 per cent.** Dissolve 100 g (NH₄)₂HC₆H₅O₇ in about 400 ml metal-free water. Shake with successive portions 0.01 per cent dithizone solution until the carbon tetrachloride phase is green. Extract the excess dithizone dissolved in the aqueous phase by shaking with successive portions of chloroform and discard the chloroform. The final extract should be colorless. Dilute the aqueous
phase to 1 liter.

Ammonium hydroxide, 1 N. Dilute 70 ml concentrated ammonia with water to 1 liter.

Dithizone (diphenylthiocarbazone), 0.01 per cent weight per volume. Dissolve 0.01 g dithizone in 100 ml carbon tetrachloride.

Dithizone, 0.001 per cent. Dilute 10 ml of the 0.01 per cent dithizone with carbon tetrachloride to 100 ml. Prepare daily and keep in a pyrex bottle covered with a dark-colored paper.

Standard lead solution, 0.01 per cent. Dissolve 0.016 g dry lead nitrate in 100 ml of solution containing 1 drop of concentrated nitric acid. This solution contains 100 micrograms lead per ml.

Standard lead solution, 0.001 per cent. Add 10 ml 0.01 per cent to about 50 ml 1 N nitric acid and make up to 100 ml with 1 N nitric acid. This solution contains 10 micrograms lead per ml.

Nitric acid, concentrated.

Nitric acid, 1 + 3, add 1 volume concentrated acid to 3 volumes water.

Water. Pass tap water through a resin demineralizer. See 'special Apparatus.'

Thymol blue indicator, 0.04 per cent. Dissolve 0.04 g of the sodium salt in 100 ml water.

Digestion and fusion rack, See 'Special Apparatus.'

Mullite mortar and pestle, diameter of mortar, 75 mm.

Balance, torsion, sensitivity, 2 mg.

1 gasoline stove.

Sieve, 80 mesh. See 'Special Apparatus.'

1 serological pipette, 0.1 ml, graduated in tenths of a ml.

1 serological pipette, 1 ml, graduated in hundredths of a ml.
1 serological pipette, 5 ml, graduated in tenths of a ml.
2 volumetric pipettes, 5 ml.
1 volumetric pipette, 10 ml.
30 pyrex culture tubes, 18 by 150 mm, marked at 2 and 10 ml.
6 graduated cylinders, glass-stoppered, 100 ml.
3 separatory funnels, Squibb type, 125 ml.
30 Stevens Extraction Sticks. See 'Special Apparatus.'

Procedure

Extraction. - Place 0.1 g of the finely ground sample in a pyrex test tube. Prepare eight samples at a time. Add 2 ml of 1 + 3 nitric acid. Allow time for effervescence from carbonates to cease. Place a Stevens Extraction Stick in the test tube and boil gently for 30 min. Cool. The solution filters into the extractor during cooling.

Estimation of lead. - Transfer the filtered solution to a clean culture tube and dilute with water to 10 ml mark. Shake and transfer a 5 ml aliquot to a 125 ml pyrex separatory funnel. Add 5 ml of 10 per cent ammonium citrate, 2 drops of thymol blue indicator and sufficient 1 N ammonium hydroxide to turn the solution distinctly yellow. Add 10 per cent potassium cyanide until the entire solution just turns blue (pH about 8.5). Add 5 ml of 0.001 per cent freshly prepared dithizone solution and shake gently for 5 sec. Drain the carbon tetrachloride (lower) phase into a 100 ml glass-stoppered pyrex graduated cylinder containing 10 ml of 0.1 per cent potassium cyanide solution. Shake the mixture for 3 sec. The unreacted dithizone is now in the aqueous phase while the pink lead dithizonate is in the carbon tetrachloride phase. From standards similarly prepared, estimate the amount of lead present.

One microgram of lead gives a weak but perceptible pink, corresponding to 20 ppm lead in the original sample, and more than 3 micrograms is difficult to estimate visually. If the first aliquot does not give a color in the suitable range, repeat using larger or smaller aliquots until a readable color is obtained.

The table given on page -64 for estimating the lead assays was made by Robert Squires, who made the lead and zinc analysis. The figures were
obtained from the literature\textsuperscript{1} on the lead method and testing against the lead standards provided by the U.S. Geological Survey.

\textsuperscript{1} Lakin, H.W., Almond, Hy, and Ward, F.N., op. cit. pg. 22.
"Table 4.--Descriptive chart of color of dithizone solution for determination of heavy metals, expressed as zinc equivalents according to Huff"

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>Volume dithizone solution (ppm)</th>
<th>Green (ppm)</th>
<th>Blue green (ppm)</th>
<th>Blue (ppm)</th>
<th>Purple (ppm)</th>
<th>Red purple (ppm)</th>
<th>Purplish red (ppm)</th>
<th>Red (ppm)</th>
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</thead>
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<tr>
<td>0.2</td>
<td>5</td>
<td>0</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>250</td>
<td>300 or more</td>
</tr>
<tr>
<td>.1</td>
<td>5</td>
<td>0</td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>500</td>
<td>600 or more</td>
</tr>
<tr>
<td>.05</td>
<td>5</td>
<td>0</td>
<td>200</td>
<td>400</td>
<td>600</td>
<td>800</td>
<td>1,000</td>
<td>1,200 or more</td>
</tr>
<tr>
<td>.025</td>
<td>5</td>
<td>0</td>
<td>400</td>
<td>800</td>
<td>1,200</td>
<td>1,600</td>
<td>2,000</td>
<td>2,500 or more</td>
</tr>
<tr>
<td>.0125</td>
<td>5</td>
<td>0</td>
<td>800</td>
<td>1,600</td>
<td>2,500</td>
<td>3,500</td>
<td>4,000</td>
<td>5,000 or more</td>
</tr>
<tr>
<td>.0125</td>
<td>10</td>
<td>0</td>
<td>1,200</td>
<td>3,500</td>
<td>5,000</td>
<td>7,000</td>
<td>9,000</td>
<td>10,000 or more</td>
</tr>
</tbody>
</table>

* Taken from U. S. Geological Survey Circular 101, pg. 15.

**TABLE IV**
<table>
<thead>
<tr>
<th>ML of soil solution</th>
<th>1.0 (green)</th>
<th>1.5 (blue)</th>
<th>2.0 (blue)</th>
<th>2.5 (purple)</th>
<th>3.0 (red purp.)</th>
<th>3.5 (purp.-red.)</th>
<th>4.0 (red)</th>
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<tr>
<td>0.75 ml</td>
<td>66-70</td>
<td>90-100</td>
<td>130-133</td>
<td>167-170</td>
<td>200</td>
<td>230</td>
<td>260</td>
</tr>
<tr>
<td>0.50 ml</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>250</td>
<td>300</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>0.25 ml</td>
<td>200</td>
<td>250</td>
<td>300</td>
<td>350</td>
<td>400</td>
<td>450</td>
<td>500</td>
</tr>
<tr>
<td>0.10 ml</td>
<td>500</td>
<td>750</td>
<td>1000</td>
<td>1250</td>
<td>1500</td>
<td>1750</td>
<td>2000</td>
</tr>
<tr>
<td>0.05 ml</td>
<td>1000</td>
<td>1500</td>
<td>2000</td>
<td>2500</td>
<td>3000</td>
<td>3500</td>
<td>4000</td>
</tr>
<tr>
<td>0.025 ml</td>
<td>2000</td>
<td>3000</td>
<td>4000</td>
<td>5000</td>
<td>6000</td>
<td>7000</td>
<td>8000</td>
</tr>
<tr>
<td>0.01 ml</td>
<td>5000</td>
<td>7500</td>
<td>10,000</td>
<td>12,500</td>
<td>15,000</td>
<td>17,500</td>
<td>20,000</td>
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For 0.3 gm sample diluted to 15 ml.

Table used in the Star project for heavy metals and zinc determinations, modified from Huff, 1952.
<table>
<thead>
<tr>
<th>Volume (ml)</th>
<th>0.5</th>
<th>1.0</th>
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<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
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<tr>
<td>0.1</td>
<td>500</td>
<td>1000</td>
<td>1500</td>
<td>2000</td>
<td>2500</td>
<td>3000</td>
</tr>
<tr>
<td>0.2</td>
<td>250</td>
<td>500</td>
<td>750</td>
<td>1000</td>
<td>1250</td>
<td>1500</td>
</tr>
<tr>
<td>0.3</td>
<td>166</td>
<td>333</td>
<td>500</td>
<td>666</td>
<td>833</td>
<td>1000</td>
</tr>
<tr>
<td>0.4</td>
<td>125</td>
<td>250</td>
<td>375</td>
<td>500</td>
<td>625</td>
<td>750</td>
</tr>
<tr>
<td>0.5</td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td>0.6</td>
<td>83</td>
<td>166</td>
<td>250</td>
<td>335</td>
<td>417</td>
<td>500</td>
</tr>
<tr>
<td>0.8</td>
<td>63</td>
<td>125</td>
<td>188</td>
<td>250</td>
<td>312</td>
<td>375</td>
</tr>
<tr>
<td>1.0</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>250</td>
<td>300</td>
</tr>
<tr>
<td>1.2</td>
<td>42</td>
<td>83</td>
<td>125</td>
<td>166</td>
<td>208</td>
<td>250</td>
</tr>
<tr>
<td>1.4</td>
<td>36</td>
<td>72</td>
<td>107</td>
<td>143</td>
<td>178</td>
<td>215</td>
</tr>
<tr>
<td>1.6</td>
<td>31</td>
<td>62</td>
<td>84</td>
<td>135</td>
<td>156</td>
<td>188</td>
</tr>
<tr>
<td>3.0</td>
<td>18</td>
<td>33</td>
<td>50</td>
<td>67</td>
<td>83</td>
<td>100</td>
</tr>
</tbody>
</table>

Table used in the Star project for the determination of lead.

**TABLE VI**
Special Notes on Laboratory Work

It was found in the Star project that the greatest source of difficulty was from contamination of the solutions used in the determinations. All solutions should be cleaned by the addition of dilute dithizone solution and shaken very vigorously for several minutes. Shaking should be continued until the addition of fresh dithizone indicates the total absence of metals. Then, to remove the dithizone used for cleaning, add carbon tetrachloride with shaking. The carbon-tetrachloride-dithizone solution settles out and is drained off. A small amount of carbon tetrachloride-dithizone solution was left in the bottom of the bottles containing reagents to insure cleanliness.

Too much stress cannot be placed upon the necessity of constantly running blanks along with the samples and the frequent checking against standards. The Hecla assayers, in addition to their own prepared standards, received a standard heavy metal and zinc solution from the U.S. Geological Survey.

The charts used to aid in estimating the parts per million of metal present will not necessarily conform with the ones prepared by others for the same test. The unavoidable slight differences in the strength of the dithizone and standard solution will cause the color series to vary somewhat. All work should be based on the set of solutions being used at the moment. When new stocks of dithizone or new standards are introduced, suitable adjustments must be made. As long as the per cent
of extraction is consistent, reagents uniform, and contamination avoided, the results should be reliable.

It may be noted that while the procedures state that the tests are not designed to determine metal contents below 50 to 100 parts per million, assays much lower than this appear on the soil assay maps. The Hecla assayers often found no indication of metal with the maximum aliquot, and so they continued with larger aliquots and additions of dithizone until a color change did occur, and by interpolation, estimated the low metal contents.

The estimation of the metal content was made visually by comparing the color of the sample solution with that of a standard when the two solutions were placed side by side in front of a fluorescent light (see Plate 3A).

The color standards fade and become useless in an hour or less. The assayer prepared a set of standard dithizone-sample solutions each morning and fixed in his mind the various colors for different key strengths, so that he could continue the rest of the day without stopping to prepare new standards.

Some workers have designed photometers to take the human factor out of reading the colors of the sample solutions. Another recom-

mended device is a mechanical shaker to facilitate mixing the dithizone with the sample solution and for mixing the reagents.  

Natural stream water obtained above Burke was found to be metal free and was used, untreated, during the first part of the laboratory work. The water of many mountain streams is suitable and, when available, saves distilling the water.

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**LIST OF MINES**

<p>| | | | | | |</p>
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</thead>
<tbody>
<tr>
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**COEUR D'ALENE MINING DISTRICT**

SHOWING MINES AND MAJOR FAULTS

FROM GORENKO, R. E., DEEP DISCOVERIES IN IDAHO'S COEUR D'ALENE MINING DISTRICT, MIN JOUR., VOL. 38, NO. 10, 1947

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