TRACE COPPER AND ZINC
IN THE CORONATION MINE OVERBURDEN

A

THESIS

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ABSTRACT

Various horizons of podsol soils developed on Pleistocene glacial sediments in the Coronation mine area were analyzed for copper and zinc by spectrophotometric means, using biquinoline-isoamyl alcohol and dithizone/carbon tetrachloride reagents, respectively.

Results indicate that major copper and minor zinc values occur in the A₀ and C horizons throughout the area; these have been largely derived from the oxidizing copper sulfide orebody. Horizons A₁, A₂ and B tend to lose heavy metals, and do not display marked anomalies. Of economic significance is the fact that the C horizon has developed an undisturbed copper anomaly directly over the orebody in excess of 100 times background value. Due to the erratic configuration of high copper concentrations in the A₀ horizon with respect to the orebody, that horizon is not considered a reliable prospecting datum.

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INTRODUCTION

General

Under certain conditions, metallic ore deposits are accompanied by primary dispersion halos of trace elements in unweathered rock surrounding the orebody, and/or secondary halos in weathered rock, soil alluvium, vegetation or water above or near the mineralized zone. In such cases chemical analysis as applied to the detection of trace elements is a valuable prospecting aid, permitting the location of mineralized zones of possible economic value.

Field work

Byers (1956) used the Bloom soil testing method (Bloom, 1955) to determine, semi-quantitatively, the total heavy metal content of soils in the Flin Flon-Amisk Lake area.

In the summer of 1955, Dr. A. R. Byers collected samples from the Coronation Mine overburden (Fig. 4). A baseline, bearing 5.34°E , had stations at 100 foot intervals from 58+00S to 66+00S; crosslines extended from 8+00E to 7+50W. Samples were collected at intervals of 100 feet or 25 feet, depending on proximity to the ore zone. A hole was dug with a spade sufficiently deep to reach the parent material or C horizon of the soil profile, usually at 24 to 30 inches below the surface. Samples were taken from each soil horizon, a portion of each sample tested in the field, and the remainder placed in a small soil sample bag and shipped to the University of Saskatchewan geochemical laboratory.

The writer did not collect any samples and did not have the opportunity of observing the soil profile, and the samples tested for their content of copper and zinc were those collected by Dr. A. R. Byers. Although 93 samples were lost, conclusions regarding the absolute copper and zinc content of the soil were drawn from the remaining 228 samples.

Principal aims

The aim of the original field survey by Byers (1956) was to determine the relative values of combined copper and zinc in horizons of the soil mantle above the Coronation Mine copper sulfide orebody. The aim of this thesis project was to determine, by spectrophotometric means, the absolute values of copper and zinc, and to compare this data with that of the original survey.

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DISCUSSION OF PODSOLS

General

The word podsol, derived from the Russian folk name sola, meaning ashes, describes the color of the eluviated A horizons of soils which form an unbroken zone in the northern forested regions of Eurasia and North America and develop under medium moisture conditions (Glinka, p. 47).

Referring to the soil profile nomenclature (Robinson, p. 84-86) which is employed in this thesis, those horizons from which material has been eluviated are called A horizons, while those enriched by the deposition of material are the illuvial or B horizons. The undifferentiated parent material lying below is the C horizon. Unaltered rock from which the C horizon has developed by weathering is referred to as the D horizon.

In the recently revised soil profile nomenclature (National Soil Survey Committee of Canada Report No. 5, 1963) the three major horizon designations A, B and C are retained, and lower case suffixes are used to specify the composition of each horizon. A portion of this system with its relation to the former system is shown below:

<u>Former</u>	<u>Present</u>
A ₀₀	L - leaf material, original structures definable
A ₀	F - partly decomposed material (fermented)
	H - decayed material, original structures undefinable (humified)
A ₁	A _h - humus accumulation, or A _{he} - humus eluviation
A ₂	A _e - (humus + clay + iron) eluviation
A ₃	AB - transition
B ₁	B _f - iron, or B _t - clay, or B _h - humus 10%, or B _{fh} - humus < 10%, or B _{fc} - cemented (iron concretions)
B ₂	B _m - no accumulation of water-soluble materials
C	C _{ca} - lime accumulation layer C - parent material

Podsolization

With a moderate degree of base unsaturation, sesquioxides become liberated by decomposition of the clay complex; humus also becomes mobile, giving rise to a loose, structureless upper horizon. Below this leached layer deposition takes place, first of humus, then of sesquioxides. Owing to the breakdown of crumb structure in the A horizons, mechanical eluviation occurs, enriching the B horizon in clay content (Robinson, p. 86).

The mechanism of podsolization is not fully understood. It is generally agreed that the sesquioxides are peptized by humus in solution. This effect is probably due to tannin, anions of humic acids, or anions of hydroxy acids formed in the decomposition of plant residues.

The mechanism of illuviation is even less clear than that of eluviation. The simplest explanation appears to be that since podsollic eluviation is usually the accompaniment of extremely acid conditions, the precipitation in B or lower horizons is due to the more alkaline character of these horizons.

Distribution of copper and zinc

Vinogradov (1959, p. 137-154) concluded that Cu and Zn tend to be concentrated in soils or soil horizons having

(1) High organic matter. Humus fixes metals and renders them insoluble and unavailable to plants.

(2) Large clay fraction. Cu and Zn are fixed within and adsorbed on clay minerals, i.e., in non-exchangeable and exchangeable positions.

(3) High pH values. Lucas (1948) showed that minimum adsorption of Cu^{2+} occurred in soil zones with the lowest pH, all other conditions being equal. Vinogradov reported that the hydroxides of Cu^{2+} and Zn^{2+} dissolve with solution pH 4.5 and 5.0, respectively.

GEOCHEMICAL SOIL PROSPECTING

General

A basic source of trace element anomalies in soils in the halo-like dispersion of these elements around weathering ore bodies and rock outcrops. By systematic trace element determination in plants and soils, detection of these halos with location of possible ore is achieved.

Dispersion halos may be divided into two groups (Fersman, 1939, p. 4) on the basis of their genetic relationship to the deposit:

1. Syngenetic. Outcropping commonly near the surface, the residual halo forms by simultaneous weathering of the deposit and the country rock.

2. Buried. Rare element concentrations are highest and have their greatest aerial extent in horizons closest to the interface between a weathering sulfide deposit and overlying material of distant origin, be it glacial, marine, lacustrine or fluvial. Determinations near the surface may provide high values due to the concentration of the rare elements in organic matter.

History

Chemical analysis as a prospecting method was first applied by Soviet geologists in 1932. Since then geochemical techniques have been applied in Russia with considerable success. In the mid-1930's Swedish investigators developed prospecting techniques using trace elements in plants. Since World War II, research has been actively undertaken on this Continent by the federal geological surveys, mining companies and universities. (Hawkes, 1949, p. 707).

Analytical techniques

Field analytical procedures must be rapid, cheap, semiquantitative, and capable of mass production. Portability of equipment is a necessity.

Of the field procedures applied to geochemical prospecting, spectrographic and colorimetric methods have been most successful to date. The former is cheaper and quicker but less sensitive than many other techniques. The popularity of colorimetry arises from its relative simplicity, adequate sensitivity, and accuracy comparable to that of the spectrographic method.

Most other analytical methods require laboratory facilities, and are presently not applicable to field surveys.

SPECTROPHOTOMETRIC ANALYSIS

Basic principles

The following notes on spectrophotometric analysis are taken from Sandell (1960) except where otherwise noted.

The wide use of colorimetric and spectrophotometric methods in analytical chemistry is based on the possibility of converting the constituent to be determined into a substance whose solution or suspension is strongly colored. Such a solution shows differential absorption of light of different wave lengths. When the percentage of light transmitted by the solution is plotted against the wave length, a transmission curve is obtained which generally shows one or two pronounced maxima or minima. Also, the percentage of light absorbed may be plotted against the wave length and an absorption curve then obtained.

The spectrophotometric analysis, light consisting of a narrow band of wave lengths is passed through a solution, and the fraction of the incident light transmitted by the solution is measured. Measurement may be subjective, that is, subject to the decision of an observer who duplicates the intensity of light transmitted through the solution by means of a comparison beam, the intensity of the beam being varied with a diaphragm or neutral wedge. In photoelectric spectrophotometric analysis, a photoelectric cell (or cells) provides an objective measurement of the light transmission of the solution.

Nomenclature

A discussion of some terms applied to spectrophotometry may be helpful.

Law of Lambert-Beer

For dilute solutions, the following relationship between intensity of incident and transmitted light in terms of concentration of the colored substance in the solution and the depth of solution is found to hold closely:

$$I/I_0 = 10^{-KCl} \quad (1)$$

in which I_0 = intensity of incident light beam; I = intensity of transmitted light beam; K = a constant, the extinction coefficient; C = concentration of the colored substance; and l = depth of solution traversed by the light.

Transmittance

The transmittance is the ratio I/I_0 , usually expressed in per cent.

Optical density

Equation (1) may be written:

$$\log I/I_0 = -KCl$$

or

$$\log I_0/I = KCl, \quad (2)$$

in which $\log I_0/I$ is called the optical density, absorbance, or extinction of solution. A plot of absorbance at constant l against concentration gives a straight line passing through the origin, if Lambert-Beer's law is followed. Similarly, the plotting of transmittance against concentration gives a transmittance plot.

Equation (2) may be expressed as follows:

$$A = \log I_0/I = \log \frac{1}{T} = abc,$$

where A = absorbance; T = transmittance; a = absorptivity; b = light path length in cm., and c = concentration of the colored species.

Sensitivity

General

The sensitivity of a color reaction is the smallest weight (gm) of substance that can be detected in a column of solution of unit cross section (cm^2). This is based on the assumption that the Law of Lambert-Beer holds to low concentrations.

There are evidently two factors involved in the sensitivity thus defined: first, the intrinsic sensitivity which is proportional to the extinction coefficient of the colored product in solution, and second, the ability of the observer, directly or indirectly, to detect small differences in the light transmittance of a solution. Definition of sensitivity in terms of the former for the wave length of maximum absorption is of little value in applied analysis, but could be used for comparative purposes.

The sensitivity of a color reaction will thus depend, according to the definition, upon the method.

Visual Colorimetry Sensitivity

The sensitivity is usually determined by using flat-bottomed tubes, one containing the blank solution, the other, variable amounts of the substance yielding the colored product together with the reagent. White light is used for illumination. Such factors as the acidity, the excess of reagent and the time of standing must be specified. The quantity of substance required to give a perceptible difference in appearance from the blank can be defined only on the basis of probability. Thus the minimum amount might be defined as that which allows a detectable difference in appearance from the blank in 90 out of 100 comparisons.

The determination of the limit thus defined would be labourious, and a less exactly defined and somewhat larger limit may be taken, namely that which in practically all cases will show a difference from the blank. (See Table 1 for some values of visual sensitivities).

For low values of weight $/\text{cm}^2$, the sensitivity determines the precision of the visual color duplication. The probability is great that the error of a single color duplication will not exceed $(s/q) \times 100$ per cent (where s is the sensitivity and q is the weight of substance in micrograms per square cm cross section of solution), as long as q is less than 15 or 20 s . When q/s is greater than 15 or 20, the precision remains constant over a wide range of q values. In other words, no useful purpose is served in working under conditions such that q/s is larger than about 20.

Photoelectric spectrophotometry

The following factors affect the sensitivity of this method:

1. The wavelength at which the determination is made. Curves of T or A vs. wavelength usually show one or more maxima or minima; a wavelength at which A is a maximum is selected.

2. The reproducibility of a measurement of T . This includes mechanical, scale reading and setting errors. Generally, photoelectric sensitivity will affect the reliability of results, particularly at low concentration levels.

It is usual to assume that most instruments will detect a difference of 0.001 in A , which corresponds to 0.2% T . Hence sensitivities are usually expressed as the concentration of substance (δ / cm^2 of cross section) which will change A by 0.001. The sensitivity of the more sensitive reactions lies between 0.001 and 0.01 δ / cm^2 , and exceptionally below 0.001 δ / cm^2 . The spectrophotometric sensitivity is 5% the visual

TABLE 1

Some visual sensitivities*

Element	Reagent	Sensitivity, δ/cm^2
Al	Aurintricarboxylate (pH 5.5)	.01
Au	p-Diethylaminobenzylidenerhodanine	.05 - .1
Be	Morin (fluorescence)	.002
Bi	Iodide	.5
Cd	Dithizone	.03
Co	Nitroso-R salt	.01
Co	Thiocyanate-acetone	1.0
Cr	As $\text{CrO}_4 =$	1.0
Cr	Diphenylcarbazide	.03
Cu	Ammonia	10
Cu	Hydrochloric Acid (9M)	.5
Cu	Diethyldithiocarbamate	.05
Fe	O - Phenanthroline	.05
Fe	Thiocyanate	.1
Ca	8 - Hydroxyquinoline (CHCl_3 , fluor).	.1
Mg	Titan yellow	.05
Mn	As MnO_4^-	.1
Ni	Bromine-dimethylglyoxime	.05 - .1
Pt	Iodide	.5
Sb	Iodide	1
V	Hydrogen peroxide	2
V	Phosphotungstic acid	1
W	Thiocyanate-stannous chloride	.3

* Sandell, p. 81

sensitivity for absorption bands in the eye-sensitive part of the visual spectrum.

Errors in spectrophotometry

A distinction must be made between random and systematic errors; the former affect precision (reproducibility of results); the latter affect accuracy (proximity to the truth). The word "reliability" may be used to cover both precision and accuracy.

For a detailed discussion, the reader is referred to Gridgeman (1952) and Faulkner (1960).

Spectrophotometer operation

The Beckman Model D.U. (Fig. 1B) consists of a light source backed by a condensing mirror which reflects light into the entry mirror, from which it is reflected through the entry slit into the monochromator housing. The light is focused by a collimating mirror onto a quartz prism where it is refracted on entry, reflected off the silvered rear surface and refracted further on emergence from the prism. Rotation of the wavelength selector alters the angle of incidence of white light on the prism. The collimating mirror again focuses refracted light onto the exit slit, where light of the chosen wavelength emerges, passes through the specimen, and causes a current gain on striking the phototube. The current gain is amplified and balanced on a null-meter by rotating the transmittance control knob.

FIG. 1 SCHEMATIC SPECTROPHOTOMETER OPTICAL DIAGRAMS

A

BAUSCH AND LOMB SPECTRONIC 20 MODEL

B

BECKMAN DU. MODEL

The first stage of the operation consists of setting the desired wavelength with the monochromator, and adjusting the exit slit width, sensitivity and dark current control until there is no deflection on the null-meter. This is necessary due to the differing output of the tungsten lamp and response of the phototube with wavelength.

As no direct determination of the transmittance of the colored solution is possible, due to the effects of the transparent container, solvents and other dissolved substances, it is usual to determine the transmittance of sample against a pure solvent or reference standard (often water) in an identical cell, after the standard has been adjusted to read $T = 100\%$.

A few samples were determined with a Bausch and Lomb 'Spectronic 20' colorimeter-spectrophotometer (Fig. 1A). White light from the tungsten lamp passes through the entrance slit and is focused by the field lens onto the objective lens. The objective lens focuses an image of the entrance slit at the exit slit after it has been reflected and dispersed by the diffraction grating. A cam rotates the grating so desired wavelengths pass through the exit slit. The monochromatic light passes through the sample contained in the test tube or cuvette and strikes the measuring phototube producing the electric signal. The latter is amplified, and transmittance read directly on a 0 - 100% scale.

Standard curves

For each substance being determined, a standard curve representing a plot of A vs. known concentrations of solutions is drawn. These are prepared under the same conditions as are sample solutions.

FIG. 2 COPPER STANDARD CURVE

(BIQUINOLINE-ISOAMYL ALCOHOL)

ZINC STANDARD CURVE DITHIZONE CARBON TETRACHLORIDE

For these plots (Figs. 2, 3) the writer made at least 5 determinations each of solutions of appropriate concentrations, and drew a smooth line through the averages of these determinations. Curves were checked whenever new reagents were prepared.

Requirements for trace analysis color reactions

High sensitivity is the most important consideration for trace element determination. Accuracy obtainable depends on sensitivity of reaction, which is a maximum for organic reagents.

Specificity, (or selectivity) of reagent, of reaction and of method are desirable. A reagent is specific if it reacts distinctively with one substance and with no others under certain conditions. For example, biquinoline is described as a specific reagent for Cu^+ because no other has been found to yield a colored complex extractable by suitable immiscible solvents. A non-specific reagent such as dithizone can be made to give a nearly specific reaction for Zn^{2+} by the addition of a buffer solution. The latter complexes the other heavy metals, alters their oxidation states and adjusts pH of solution to favor formation of zinc dithizonate complex. Specific methods are attainable only when certain elements are not present in sufficient amounts to interfere.

A stable and reproducible color is desirable. Variables to be controlled include pH of the medium, excess of reagent, time of preparatory shaking, and standing time before measurement of the color intensity. Organic reagents usually give less stable products than do the inorganic, but often are sufficiently stable to furnish highly accurate results.

Adherence to the Lambert-Beer law makes a system more convenient to use and permits greater accuracy, but is the least important of the desiderata.

Advantages of absorptive spectrophotometry

Spectrophotometric methods have a number of advantages over the visual colorimetric method:

1. Sensitivity is increased by measuring solution absorption at the wavelength of minimum transmission.
2. With a photoelectric cell measurements may be made in the ultraviolet or infra-red ranges.
3. The effect of foreign-colored substances can be avoided or minimized by working at suitable wave lengths.
4. Higher instrument precision is available.
5. For large-scale analysis, objective spectrophotometric methods are more rapid and less fatiguing than the subjective colorimetric methods.
6. A comparison of spectrophotometric with spectrographic methods shows this disadvantage: relatively extensive separations in spectrophotometric procedures may retain interfering elements, lose some of the desired constituent, and be laborious. On the other hand the spectrophotometric method becomes absolute when foreign substances are eliminated. In spectrographic analyses separations are rarely made, and the accuracy may depend upon sample composition and accuracy of the standard.
7. The optical density of a solution may be measured more precisely than the position of a line on a photographic plate.

The two methods show similar sensitivities, that for the dithi-
zone spectrophotometric method being $\leq 10^{-4}$ mg, and that for spectro-
chemical methods from 10^{-4} to 10^{-6} mg. If a large amount of sample is
treated spectrophotometrically, its concentration sensitivity may counter-
balance the higher absolute sensitivity of a spectrographic method, which
ordinarily uses small samples.

Copper determination

General

For a general discussion of the methods used for the determination
of copper the reader may refer to Almond (1955).

The 2,2' Biquinoline (2-2' diquinolyl, cuproine) method, used in
this thesis project, was first reported by Breckenridge (1939) as being
specific for Cu^+ . Hoste (1950) stated that biquinoline was superior to
dithizone as a reagent for Cu^+ determination. Hoste et al (1953) described
the determination of Cu^+ in many materials, using biquinoline. Cheng and
Bray (1953) used the reagent to determine Cu^+ in soils, reporting the Cu
complex extractable into isoamyl alcohol with a maximum absorption at
540 $m\mu$, and interference from: citrate, concentrated NH_4OH , ethylene
diaminetetraacetate, oxalate, cyanide, thiosulfate, soluble silicate,
bromate, iodate, ferricyanide and cyanate. Almond (1955) modified the
technique for sample decomposition and found biquinoline in isoamyl
alcohol suitable for Cu^+ colorimetry of soils and rocks in the field.

The advantages of the biquinoline method may be summarized as
follows:

1. pH of the aliquot taken is more easily adjusted.
2. The time required for shaking the buffered solution with reagent is less.
3. The reagent is specific for Cu^+ .
4. The reagent and complex are quite stable at room conditions over periods of several months. (Almond, 1955).

Biquinoline, having a sensitivity of 0.010, is 100 times more sensitive to Cu^+ than ammonia, $2\frac{1}{2}$ times less sensitive than sodium diethyldithiocarbamate, and 4 times less sensitive than dithizone. (Sandell, 1959).

According to Hoste (1950), Cu^+ forms intense purple-colored complexes with compounds containing two pyridyl groups, a pyridyl and a quinolyl group or two quinolyl groups linked in 2,2 position. These complexes are insoluble in water, but soluble in organic solvents, and contain in solution two molecules of the organic reagent to one Cu^+ ion. The compound forms a sensitive stable complex in acid medium, which may be represented as follows:

Sandell (1959) reported that isoamyl alcohol was the best extractant of the biguinoline-Cu complex.

The procedure followed by the writer for Cu determination of soils is essentially that outlined by Almond (1955) for soils and rocks: A pyrosulfate fusion of a powdered soil or rock sample followed by extraction into HCl dissolves essentially all of the Cu. (The fusion method gives a total heavy metal content of the soil. Both the adsorbed Cu compounds and metallic Cu present in the silicate structures of the clays are brought into solution. This has the undesirable feature of including metals not representative of ore minerals in the area, but is preferable to the HNO_3 digestion method, in which only about 80 per cent of exchangeable Cu is dissolved from soil particles). Neither sulfate nor chloride interfere with the biquinoline method, so this treatment is suitable. Hydroxylamine hydrochloride is added to an aliquot to reduce Cu^{2+} to Cu^+ , tartrate is added to complex Fe^{3+} and Al^{3+} , and acetate to buffer the solution. The copper-biquinoline complex is then extracted into isoamyl alcohol. Field and laboratory techniques differ only in that in the former, field stoves are used instead of Bunsen burners, measurement of volumes is approximate rather than exact, and estimations are made by comparison with a standard series rather than instrumentally.

Zinc determination

General

Before being replaced by dithizone, sulfide precipitation methods (Sandell, p. 941) were commonly used for zinc determination.

The writer employed the dithizone method, in which Zn reacts readily to form the primary dithizonate which is soluble in carbon tetrachloride (CCl_4) giving a solution of bright red color. Carbon tetra-

chloride is a superior solvent because of rapid extraction.

A visual colorimetric method devised by Bloom (1955) has been used quite successfully for Zn, Cu and Pb estimation by Riddell (1953) and Byers (1956). The method involves extraction of total heavy metals with a cold ammonium citrate solution in the presence of dithizone dissolved in xylene or carbon tetrachloride. After shaking, the xylene above the aqueous phase varies through green, blue, purple, red or brown, as the amounts of heavy metals increase. If the original color in the xylene layer persists when potassium cyanide is added, the heavy metal in the sample is lead. A brown color in the xylene layer indicates a predominance of copper. If the tests for copper and lead are negative, the original color may be assumed to be caused by zinc.

Discussion of dithizone and the Zn- dithizone procedure

(The following notes are from Sandell, 1959). Diphenylthio-carbazone, or dithizone,

was first prepared by Emil Fischer, who in 1882 noted its reaction with heavy metals to give brilliantly-colored products. In 1925, Hellmut Fischer showed its great value in determining various heavy metals.

The sensitivity of dithizone methods approaches and sometimes exceeds that of spectrographic methods. 0.0016 micro-grams ()/cm² has been found for log I₀/I = 0.001, with a green filter.

In hydrocarbons dithizone is only slightly soluble: in carbon-tetrachloride about 0.05 gm/100 ml. Dilute solutions of dithizone in carbon tetrachloride (as well as other organic solvents) are green, but more concentrated ones are dichroic (red in transmitted light, green in reflected light).

When a solution of dithizone in an immiscible organic liquid is shaken with an aqueous solution of a reacting heavy metal, an internal complex-dithizonate is formed, which generally is soluble in the organic solvent, to which it imparts a violet, red, orange or yellow color. Dithizone and the dithizonates are virtually insoluble in neutral and acid aqueous solutions.

Some metals can replace either one or both of the acid hydrogens of dithizone to form 2 different complexes. These were called Keto and Enol forms by H. Fischer, but are better named primary and secondary dithizonates. According to Fischer, the hydrogen of the imide group of dithizone is replaced by the metal to give the primary dithizonate, and the hydrogen of the sulfhydryl group of the thiol form of dithizone is also replaced to give the secondary dithizonate as follows:

The primary dithizonates of all reacting metals exist; the secondary dithizonates of many reacting metals are unknown. Cu, Ag and Hg readily form both primary and secondary dithizonates. The primary complexes are preferentially formed in acid solution, and the secondary in alkaline medium or with a deficiency of dithizone. A secondary dithizonate can be transformed into the primary form by treatment with dithizone and/or acid:

Although dithizone is non-specific, the reaction may be made quite specific for certain metals by resorting to one or more of the following devices:

1. Adjusting the pH of the solution to be extracted.
2. Altering the oxidation state of interfering metals.
3. Adding a reagent to complex other interfering metals.

Dithizone extractions can be carried out by mono- or dicolor (mixed color) methods. In the former, the metal is extracted from aqueous solution with successive portions of dithizone in carbon tetrachloride or chloroform which is treated with a weakly basic solution to remove excess dithizone. Sources of error are involved: if wash solution is too basic, some dithizonate will dissolve; if wash solution is not alkaline enough, free dithizone will remain in the solvent.

In the mixed-color method, excess dithizone is allowed to remain in the organic solvent with the dithizonate. With a spectrophotometer, one may measure the absorption of light by the metal complex (usually preferred) or by the excess of dithizone. In carbon tetrachloride, the wavelengths of maximum absorption for dithizone and primary zinc dithizonate are 620 and 535, respectively.

Dithizone is rapidly oxidized to diphenylthiocarbadiazone atmospherically, especially under the influence of light, while Fe^{3+} oxidizes it readily in basic solutions. The first product can be reduced easily by reducing agents such as hydroxylamine hydrochloride and SO_2 , but further

oxidation products are permanent. Since both dithizone and dithizonates are light sensitive, the former should be stored in a cool dark place in foil wrapped pyrex bottles, and the latter determined without delay.

The zinc determination procedure followed by the writer was developed by Mr. Faulkner. An aliquot of solution previously prepared for Cu determination is further diluted and treated with hydroxylamine hydrochloride, reducing Fe^{3+} to Fe^{2+} , to prevent oxidation of dithizone. NH_4OH is used to neutralize the solution and precipitate $\text{Fe}(\text{OH})_2$. The latter is dissolved by acetic acid buffer of pH = 5.5 which contains citric acid to complex Al_2O_3 , and H_3PO_4 to complex Fe_2O_3 . Sodium diethyldithiocarbamate is added to prevent interference by Cu and other heavy metals. Dithizone, 0.001% W/V in carbon tetrachloride, extracts Zn^{2+} from the solution.

Sample preparation

The soil samples were prepared for analysis in a separate room to avoid dust contamination of the laboratory. An alumina hand mortar was cleaned before being used to pulverize clay samples. Organic samples were ashed in porcelain dishes over Bunsen burners. A portion of each sample was passed through stainless steel sieves which were cleaned with an air jet after each sieving. A 2 gm portion of the minus-100 mesh fraction was placed in a screw cap culture tube.

Prior to fusion of samples with potassium pyrosulfate, the components were mixed with an aluminum wire to prevent soil from being blown out of the tube by a non-uniform fusion process.

To stop gross zinc contamination, it was found necessary to cover the

wire pipette rack with polyethylene tubing, and a glass pipette used for buffer solution was substituted for a syringe pipette.

The importance of keeping glassware scrupulously clean cannot be overemphasized by the writer.

TESTS OF SOIL FROM THE CORONATION MINE OVERBURDEN

The Coronation Mine Area

Location and general character

The Coronation mine is located at latitude $101^{\circ}59'48''$ and longitude $54^{\circ}35'04''$ on the northeast shore of Phil Lake, which is 13 miles south-southwest of Flin Flon. It is serviced by a gravel road and mine railway from Flin Flon. The mine site, formerly covered by spruce and poplar trees, was cleared off to provide space for mining operations. Lying in an area immediately north of the Precambrian-Palaeozoic contact, it is characterized by a few rounded outcrops protruding 10 to 20 feet through muskegs and glacial deposits. Glacial striae and drumlins in the area indicate ice movement from north to south.

Regional geology

In the Amisk-Wildnest Lakes area, which lies directly to the west of the Coronation mine, all consolidated rocks, except for Ordovician dolomite and sandstone, are of Precambrian age. The regional geological setting of the area may be seen best on Map 850A, Geological Map of Manitoba and Map 895A, Geological Map of Saskatchewan, of the Geological Survey of Canada. The stratigraphy of the area is indicated in Table 2. The regional structure consists of a wide compound "granite" batholith trending roughly east-west and flanked by two roughly parallel belts, the inner of gneiss and the outer of sedimentary-volcanic complex, on either side. On the south flank, the gneisses (Kisseynew) adjacent to the batholith are largely derived from sediments and volcanic rocks. South of the gneisses is a belt of basic to intermediate volcanic rocks (Amisk) unconformably overlain by isolated areas of conglomerate and arkosic sediments (Missi).

FIG. 4- KEY GEOLOGICAL MAP, CORONATION MINE AREA

100 0 100 200 300

SCALE IN FEET

LEGEND

	Ore body, 150' level		Flow banding (dip known)
	Qtz/Qtz-felds. porph.		Pillow structure (top known)
	Feldspar porphyry		Lineation (plunge known)
	Basic mass/emyg. lavas		Jointing (vertical, inclined)
	Pillow lavas		Outcrop
	Flow Breccia		Building
			Shaft
			Railroad

TABLE 2

Table of Formations, Amisk-Wildnest Lakes Area

ERA	PERIOD	NAME	DESCRIPTION
Cenozoic	Recent and Pleistocene	Alluvium, glacial deposits	Sands, gravels, clays
UNCONFORMITY			
Palaeozoic	Ordovician	Red River Fm. Winnipeg Fm.	Mottled and non-mottled dolomites Yellow to red calcareous sandstone.
UNCONFORMITY			
Precambrian		Post-Tectonic	Granodiorite to pyroxenite, aplite, and pegmatite.
		Syntectonic	Pegmatite; foliated and massive biotite-microcline granite, hornblende and/or biotite granodiorite.
			"Quartz-eye" diorite Pyroxenite, peridotite; derived serpentine and talc-magnesite rocks. Gabbro, diorite, gabbroic pegmatite. Porphyritic meta-gabbro and derived chlorite-carbonate schists.
		INTRUSIVE CONTACT	
		Kisseynew Group	Quartz, granulite, biotite and/or hornblende gneiss, amphibolite, and garnetiferous facies of these rocks, derived from Missi, Amisk and minor basic intrusive rocks.
		GRADATIONAL CONTACT with PROBABLE FAULT CONTACT IN PLACES	
		Missi series	Arkose, greywacke, minor quartzite and conglomerate; derived gneiss and schist.
		UNCONFORMITY	
			Porphyries, rhyolite to andesite.
		INTRUSIVE CONTACT	

TABLE 2 (continued)

		Amisk Group	<p>Greywacke, quartzite, conglomerate, minor argillite, interbedded volcanic rocks; derived schists and gneisses. Acidic to intermediate lavas, flow breccia and pyroclastic rocks; minor undifferentiated acidic to basic intrusions and basic volcanics; derived schists and gneisses. Massive to pillowed basic lavas, flow breccia and pyroclastic rocks; minor amounts of undifferentiated acidic and basic intrusions, and volcanic rocks; derived schists and gneisses. (Byers and Dahlstrom, 1954)</p>
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All three groups are intruded by granodiorites and some granites of batholithic dimension. Small amounts of basic and ultrabasic intrusions cut the Amisk group particularly, but intrude the other two groups as well. There are three intrusive sequences; one is pre-Missi, and the other two are post-Missi in age. The only pre-Missi intrusive rocks are dikes, sills and small irregular masses ranging in composition from granite to gabbro, which are considered the intrusive equivalents of the Amisk volcanic rocks.

Structures in both the Kisseynew gneisses to the north and the less metamorphosed Amisk group and Missi series are complex. Since there is no major time break between the latter two, and because the Kisseynew is regarded simply as their metamorphosed equivalent, all three are considered as being folded during the same orogeny. Faults and shears include major breaks which relieved regional stress, and minor breaks which cut post-tectonic intrusions and displace older shear zones. Major faults striking west of north have apparent left-hand strike-slip movement. (Byers and Dahlstrom, 1954).

Coronation mine geology

The Coronation ore body is a replacement of part of an essentially concordant shear zone in a sequence of metamorphosed volcanic rocks consisting of relatively massive, altered dacites, andesites and andesite breccias, with some pillow lavas and minor fragmental rocks. (Fig. 4).

The orebody consists of varying amounts of massive to disseminated pyrite, pyrrhotite and chalcopyrite with minor amounts of sphalerite and some magnetite, in a series of ore shoots within a zone 900 feet in length, 1000 feet in depth and up to 200 feet wide. The strike of the zone is

northwest and the dip is 75° southwest. The zone coincides with a contact between andesite breccia in the footwall, and dacite in the hanging wall. Top determinations near the mine indicate the volcanic strata are overturned.

For purposes of description, the orebody can be divided into three sections:

1. North:- mostly massive and vein-like sulfides of relatively high grade. Wallrock alteration is slight.
2. Central:- massive and disseminated sulfides of low or marginal grade.
3. South:- disseminated sulfides of moderate grade. Each section has an overall plunge of 80° S., corresponding roughly to the plunge of lineations, elongated fragments and minor structures of the volcanics in the area.

Mineralization is markedly related to shearing. Movement on the shear zone is left-hand, with slickensides plunging 10° S.S.E., and has been estimated at no more than 50 feet. Most of the movement has been localized in a hangingwall and footwall shear zone separated by 100 feet to 150 feet of variously affected country rock.

In the north section, most shearing is confined to the hanging-wall and footwall, with only limited shearing and alteration of the intervening rock. The mineralization consists of two replacement veins of massive sulfides in the hangingwall and footwall shears, and very minor but widespread disseminated and veinlet sulfides in between.

The central zone is somewhat more sparsely mineralized, but the sulfides are more uniformly distributed with some concentrations on the extensions of the hangingwall and footwall shear zones.

In the south section, the shearing is extensively dispersed throughout the width of the ore zone, and into the country rocks on either side. The mineralization is likewise dispersed and varies from occasional massive parts to more typical stringers and disseminated sulphides.

The boundary between sections is sharp to gradational.

The wallrock alteration is complex, and consists mainly of varying development of chlorite, hornblende, garnet and tremolite/actinolite with lesser amounts of epidote, cordierite, anthophyllite and carbonates. Some minerals such as quartz and feldspars, present in the original rocks, persist with minor alteration and recrystallization.

In the ore zone, gangue minerals as such are almost wholly absent, and occur as minor fracture fillings of quartz, quartz-epidote, quartz-carbonate or carbonate which may be the same age as, or later than, the ore. The extent of alteration, and the gangue distribution are, like the sulfide mineralization, closely dependent on the shearing. In the wider sections of the shear zone, alteration is extensive, often coarse-grained and skarn-like.

On a regional scale, the mine shear zone appears to be related to the northerly-trending Ross Lake system. One fault of this system to the northwest of the mine has been found, upon drilling, to contain some chalcopyrite and iron sulfides. Drilling has traced the extension of the mine shear zone, a single zone of sheared rock with disseminated iron sulfides, to the northwest, it appears to follow an S-shaped flexure in the volcanic rocks. The south extension of the mine shear zone is very poorly defined, and is lost near the contact of the volcanics with part of the Renard Lake syntectonic granodiorite. The field relationships and the

displacement in the mine shear zone are consistent with it being an 'en echelon' or similar type of branch fault related to a main northerly-striking fault.

Within the mine area itself, there is a set of pre-ore conjugate joints and faults of slight displacement, one set roughly parallel to the ore body, the other roughly at right angles, dipping north at shallow angles. There are a few post-ore faults and joints, mostly horizontal and of the shrinkage or tension type, dying out rapidly away from the ore zone.

Within the ore zone the structure increases in complexity from north to south. The most prominent feature of the south section is a series of mineralized ribbons, with development of curved fractures and joints indicating possible localized rotation.

Pre-ore intrusions are fairly common, mostly as small, very irregular bodies and dike-like masses, including coarse diorite and quartz-feldspar porphyry. Post-ore intrusions are present as small dykes of dark, very fine-grained material of intermediate composition. (Mr. E. L. Faulkner, personal communication.)

Nature of the overburden

Overburden in the area consists of Pleistocene glacial sediments of three general types:

1. Glacial deposits of till, largely sandy with minor clay.
2. Glacio-fluvial or outwash deposits of sand and gravel (local).
3. Glacio-lacustrine deposits of clay, silt and sand, often well-bedded.

The glacio-lacustrine deposits are the most widespread.

The above sediments wherever they occur at the surface have undergone podsolization. A generalized profile is shown:

- A₀ - Partly decomposed leaf matter; may be disturbed or burned. (0" - 5" Thick.)
- A₁ - Thin or absent, frequently represents a mixture of organic matter, ash and mineral soil where A₀ has been burned. (0" - 1" thick.)
- A₂ - Light grey with pale brown streaks; often sandy; horizontal platy structure. (1" - 10" thick.)
- B - Greyish brown; often with moderate amount of CaCO₃, especially near the base; often blocky and nutty. (6" - 25" thick.)
- C - Generally some shade of grey; structure of parent material. (Byers, 1956.)

Field colorimetry results

From a study of over 100 profiles in the Flin Flon-Amisk Lake Area, Byers concluded:

1. The A₀ horizon contains the greatest concentration of heavy metals, but their erratic distribution would render the material of no value for detecting a weak geochemical anomaly.
2. With the exception of soils over ore-zones in which values were high, the A₂ horizon is always low. High values could usually be accounted for by contamination by organic material from the A₀ horizon.
3. Although the B horizon contains slightly more heavy metals than the C horizon, the difference would not greatly affect a geochemical anomaly. Sampling the parent material at a uniform depth below the surface gives satisfactory results and requires less time.
4. There is a close correlation between clay fraction and percentage of heavy metals in the sample.

5. Barren sulfide bodies and other electrical conductors can be differentiated from those containing Cu and Zn of sub-ore to ore grade. The method can be best used to test a geophysical anomaly or a known favorable structure.

The method employed by Byers was the Bloom Method.

Laboratory spectrophotometry results

Precision considerations

The following discussion will serve to compare the reproducibility (precision) of the copper-biquinoline and the zinc-dithizone methods:

The confidence limit (Youden, 1951) is defined as the limit within which the average of a number of quantitative determinations may lie, e.g., for a confidence of 95%, 95 out of 100 determinations will probably lie within predictable confidence limits, which decrease with increasing number of measurements.

Five copper determinations for sample 64+00S, 4+50W, 12" below A_0 , were made and the confidence limit found as follows:

D = deviation

V = variance

m = average deviation for small sets

s = standard deviation for small sets

<u>Cu ppm</u>	<u>D. from Ave.</u>	<u>D²</u>
51.5	4.3	18.5
52.3	3.5	12.2
56.0	0.2	.04
58.4	2.6	6.75
<u>61.0</u>	<u>5.2</u>	<u>27.0</u>
Ave. = 55.8	m = 3.27	

$$V = \frac{D_1^2 + D_2^2 + \dots + D_n^2}{n - 1} = 14.9$$

$$S = \sqrt[2]{V} = 3.86 = 1.18 \text{ m}$$

(Theoretically, $S = 1.25 \text{ m}$).

i.e. on the average, 2 of every 3 measurements will deviate from the value of 55.8 by $< | 3.86 |$ ppm.

$$\begin{aligned} \text{The 95\% confidence limits} &= 55.8 \pm 2.78 \times \frac{5}{\sqrt{5}} \\ &= 55.8 \pm 4.78. \end{aligned}$$

where 2.78 is the factor for confidence limit at 95% probability and a set of 5. (Youden, p. 19).

Similarly, for zinc:

Four determinations for sample 64+00S, 3 + 75W, 1.7' = 2.0' below the surface, were: 16.6, 13.3, 15.8 and 35.1. By assuming a lower confidence limit (90%) with a confidence limit factor of 2.35, calculations similar to the above provided this information:

$$\begin{aligned} \text{Ave.} &= 20.4; m = 7.55; V = 100.67; S = 10.03; 90\% \text{ confidence} \\ \text{limit} &= 20.4 \pm 11.7. \end{aligned}$$

The zinc-dithizone method is not as precise as the copper-biquinoline method, because it involves twice as many reagents and a more involved procedure, and the sensitivity is approximately 6 times that of the copper-biquinoline method.

Discussion of Results

Referring to figs. 5, 6, 7 and 8 and Table 3, the following statements concerning average values for copper and zinc may be made:

1. The A_0 horizon contains about 8 times as much copper and 3 times as much zinc as each of the lower horizons, concentrations in the latter being of the same order of magnitude.

2. Concentrations of copper and zinc decrease from A_0 to B in the soil profile, with C containing somewhat more metals than B. The Cu:Zn ratio behaves similarly:

A_0 , 14.2; A_1 , 9.5; A_2 , 8.8; B_1 , 5.5; C, 5.8.

It should be noted that, from a study of 100 profiles, Byers found the B horizon to contain more heavy metals than the C horizon. This was due to the fact that the Bloom method detected most of the Cu adsorbed on clay particles, but did not detect the Cu present in the clay silicate structures.

Soil pH may have been an important factor in the manner of Cu concentration. Cu and Zn hydroxides, which would ordinarily be preferentially concentrated in the layer with the largest clay fraction (the B horizon), would be unstable if the pH of that layer was less than 4.5. The abundant occurrence of calcium carbonate in the parent material indicates a high content of alkaline earths, favorable to the precipitation of Cu and Zn hydroxides.

3. Horizon A_2 contains essentially the same amounts of Cu and Zn as A_1 .

4. Zn values are more constant than Cu values, and are related to Cu anomalies. Zn values may reach several 10's of ppm, but are usually less than 10 ppm.

5. Background values of Cu and Zn increase slightly toward the orebody.

The outstanding anomaly on the 64+00S line at 4+00W is of particular interest. Located directly over the orebody, the halo is as wide (100', along the 4+00W line) as the orebody itself, and does not vary in size or change position in the profile except in the A₀ layer, where values are high and widely dispersed. The C horizon shows the highest anomaly of greater than 100 times background value, while upper horizons show 'highs' of less than 10 times background level.

It should be noted that, in several profiles over the ore zone, the Bloom method indicated that the B horizon contained more heavy metals than the C horizon. Observing that the long axis of the anomaly was almost parallel to the direction of glacial movement, . . . Byers concluded that chalcopryrite, sphalerite and their oxidation products were incorporated in the till by glacial action. The present writer's detection of more copper and zinc in the C than in the B horizon is due to the use of a hot HCl solution which extracted all copper from the samples. The Bloom method, which used a cold ammonium citrate solution, extracted most of the copper which was adsorbed on soil particles but detected only a fraction of the copper present in copper sulfide and silicate compounds.

Although the 63+00S line does not pass over the orebody or display marked anomalies, the A₂, B and C horizons show a slight increase in copper content downslope from 3+50W. The A₁ horizon shows one high value at 3+50W which is likely due to contamination. A₀ values are high and show no relation to the orebody.

Background metal values are everywhere less than average values in the country rock (H.W.: 127 ppm Cu, 133 ppm Zn; F.W.: 144 ppm Cu, 80 ppm Zn. Samples were taken 150' and 100', respectively, from the orebody. (Personal communication, Mr. E. L. Falkner.)

Noting the coincidence of the C horizon anomaly, (Fig. 6) picked up on line 64+00S (Byers, 1956) with the anomaly located by spectrophotometric means, it is evident that the Bloom method is quite adequate for locating ore deposits of this type.

FIG. 5- VARIATION IN Cu AND Zn,
CORONATION MINE SOIL PROFILE

63+00 S LINE

FIG. 6 - VARIATIONS IN Cu AND Zn (ln) ~ CORONATION MINE SOIL PROFILE ~ 64+00 S LINE

FIG. 7 - BAR GRAPH OF Cu AND Zn, LINE 63+00 S

*contamination likely

FIG. 8 - BAR GRAPH OF CU AND ZN, LINE 64+00 S

TABLE 3 - Averages of copper and zinc analyses for the Coronation Mine soil*

Horizons Profiles	A ₀		A ₁		A ₂		B		C					
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn				
	No	Ave ppm	No	Ave ppm	No	Ave ppm	No	Ave ppm	No	Ave ppm	No	Ave ppm		
58+00S											2	40.2	2	9.6
60+00S											12	27.4	12	5.3
62+00S	2	52.7	2	5.2	2	51.8	2	2.2			2	30.6	2	4.2
62+15S	1	22.4	1	3.5	1	36.6	1	7.8			1	7.7	1	4.8
63+00S	13	453.0	13	34.8	10	43.8	10	4.9	5	47.8	6	4.0	12	25.7
63+50S									1	43.0	1	6.4		
64+00S	8	279.3	7	12.3	6	79.7	8	7.4	3	73.5	3	7.9	7	42.8
64+15S	1	90.5	1	5.7	1	67.0	1	0.9	1	29.8	1	6.1		
64+25S	1	75.9	1	12.4	1	8.4	1	8.4	1	-	1	5.1		
65+00S													17	29.5
66+00S													1	51.4
Totals	26	8413.2	25	570.2	21	1132.5	23	130.1	11	532.3	12	65.5	22	676.8
Averages	324.0 / 22.8		53.9 / 5.7		48.5 / 5.5		30.8 / 5.6		37.2 / 6.4					

No. - Number of samples

* Background values only

CONCLUSIONS

Copper and zinc are concentrated in the A_0 horizon to a high and in the C horizon to a lesser degree, and tend to be leached from the A_1 , A_2 and B horizons.

The A_0 horizon contains a high amount of Cu and Zn in its organic material. High contents of Cu and Zn in the A_0 layer occur throughout the mine area, indicating that the A_0 layer would not be a reliable prospecting datum.

The tendency for the podsol in the mine area to contain more copper and zinc in the C layer than in the B layer is counter to published data from the Flin Flon-Amisk Lake area (Byers, 1956) and elsewhere (Vinogradov, 1959). Over the Coronation orebody, this tendency reflects the ability of the acid extraction method, used by the writer, to detect copper in clay silicate structures, copper sulfides and oxidation products which were present in the parent material. Elsewhere in the mine area, the writer considers the higher copper and zinc content of the C horizon to be the result of a difference in pH between B and C, the C horizon being more basic and thus favoring the formation of copper and zinc hydroxides.

Since the country rock contains copper and zinc in essentially equal amounts, one would expect the soil to show small Cu:Zn ratios if significant quantities of metal were contributed by the country rock. That heavy metal content of the soil has largely been derived from the orebody is indicated by the increase of those metals toward the orebody, and by the high Cu:Zn ratios of all horizons, which reflect the high proportion of chalcopyrite to sphalerite in the orebody.

The C horizon is considered the most favorable prospecting datum because:

1. It consists of fairly uniform material, and is usually located at depths of 2.0' to 2.5' below the surface. Upper horizons tend to be discontinuous and heterogeneous regarding mechanical properties.
2. The C horizon has not been disturbed, or contaminated by organic material due to its depth in the soil profile. Upper horizons commonly contain large amounts of copper which show no systematic relation to the orebody.
3. It displays the highest anomaly with the copper and zinc derived from the orebody forming a "buried halo".

In the initial stage of any soil survey of this nature, all horizons should be sampled in the event that variance of groundwater conditions and the nature of the soil itself result in anomalous heavy metal occurrence in some horizon(s) other than C. Sampling at 25 foot intervals along lines spaced 50 feet apart would provide satisfactory control.

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APPENDIX A

Apparatus

- 1 - balance, trip, 200 gm.
- 1 - balance, acc. to 0.001 gm.
- 1 - oven, drying
- 1 - water bath
- 1 - Beckman D.U. Spectrophotometer/1 - Bousch and Lamb spectronic
20' colorimeter.
- 1 - Bunsen burner
- 1 - set of sieves, stainless steel, to minus 100 mesh
- 1 - spatula
- 1 - aluminum/steel wire loop
- 1 - pipette rack (enamelled/polyethylene-covered).
- 1 - separatory flask rack, wooden
- 1 - motor, 110-volt, "mixmagster", for mixing sodium dithiodiphenyl-
carbamate solution.
- 1 - capsule magnet
- 1 pr. - grips, test tube
- 1 - flint lighter
- 1 - still, H₂O
- 6 ft. - tubing, $\frac{1}{4}$ ", polyethylene
- 2 - resin tubes, polyethylene, 1" x 8"
- 300 - test tubes, 16 x 150 mm.
- 1 - rack, test tube, polyethylene
- 6 - flasks, separatory, 60 ml.
- 15 - flasks, graduated, 25 ml. class 'A'
- 3 - pipettes, glass, 5 ml.
- 1 - pipette, glass, 4 ml.
- 1 - pipette, glass, 10 ml.
- 1 - pipette, glass, 1 ml, grad. to 0.1 ml.
- 1 - pipette, syringe, 5 ml.
- 1 - cylinder, glass, graduated, 1-1.
- 1 - cylinder, glass, graduated, 100 ml.
- 1 - beaker, glass 1-1.
- 1 - beaker, glass, 500 ml.
- 1 - distilling flask, 1 l., with condenser and accessory bottle
- 1 - bottle, 500 ml., wash, polyethylene
- 2 - bottle, 1 gal. polyethylene
- 2 - bottle, 1 l., polyethylene
- 2 - bottle, 1 l., pyrex, foil-covered
- 1 - bottle, 1 l., glass
- 12 - funnels, polyethylene
- 5 boxes - filter paper, No. 40 (Whatman)

APPENDIX B

Reagents for copper determination

Biquinoline (0.02 per cent, W/V). Dissolve 0.2 gm of 2-2'-biquinoline in 900 ml of isoamyl alcohol by warming in a beaker on a hot plate. Cool, make up to 1 liter with isoamyl alcohol in a 1-liter volumetric flask. The reagent in alcohol should be colorless. If the solution is yellow, the reagent is impure and should not be used.

Buffer solution. Dissolve 400 gm of sodium acetate and 100 gm of sodium potassium tartrate in 1 liter of water. To 10 ml of solution in screw cap culture tube add about 50 mg hydroxylamine hydrochloride, mix to dissolve, add 1 ml of 2,2'-biquinoline reagent. Screw cap in place and shake 2 minutes. If no pink appears in the organic phase, the buffer is free of Cu contamination.

Hydroxylamine hydrochloride

Potassium pyrosulfate

Hydrochloric acid (1:1). Add 500 ml concentrated hydrochloric acid to 500 ml metal-free water.

Standard copper solution 0.01%. Dissolve 0.2 gm of clear uneffloresced crystals of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water, add 70 ml of concentrated HCl, dilute to 500 ml with water. One ml contains 100 micrograms of copper.

Demineralizing resins.

Distilled water is passed through mixture of amberlite IRA 400 and amberlite IR 120, in the ratio of 2:1 (wet wt.).

APPENDIX C

Reagents for Zinc Determination

(Mr. E. L. Faulkner, M.Sc. thesis and person communication)

Carbon Tetrachloride. Reflux the reagent grade material with 10 per cent NaOH for two hours, decant and shake 5 minutes in separatory funnel with 10 per cent hydroxylamine hydrochloride. Wash with water, separate sharply and dry overnight with calcium oxide. Distill from a little fresh calcium oxide, discarding the first few mls of distillate.

To recover, separate the contaminated solvent from any aqueous phase and shake with 10 per cent of its volume of concentrated H_2SO_4 . Separate and wash the solvent with water to remove acid, then treat as for the reagent material.

NOTE: Several drops of bromine were added to each gallon of reagent CCl_4 as received from suppliers, and allowed to stand for several days. Zinc impurities were sufficiently low, and zinc is a weak "sulfide former", so ZnS_2 interference did not occur. However, copper, which forms relatively insoluble sulfides readily, was present, necessitating the above bromine treatment to fix copper in solution.

Dithizone. Reagent is ordinarily pure enough for most purposes if a 0.01 percent W/V solution in CCl_4 gives only a faintly yellow colored layer on shaking with an excess of pure dilute NH_4OH . If the CCl_4 layer is a strong yellow, or pink, then the dithizone may be purified by re-crystallization from chloroform or by any of the methods given by Sandell. (0.01% W/V). Dissolve 0.025 gm dithizone in 250 ml CCl_4 (4 by shaking vigorously for 30 minutes.)

Hydrochloric acid. Prepare pure HCl by dropping reagent grade concentrated HCl into concentrated H_2SO_4 . The mixture is heated whenever the reaction slows down. Dissolve gas in cooled purified water until a strength of app. 9 M. is attained.

Ammonium hydroxide. Dissolve pure NH_3 gas, from a heated reagent grade NH_4OH , in purified water.

Buffer solution. To 100 ml H_2O add 5 gm citric acid, 5 ml phosphoric acid, and 85 ml concentrated acetic acid. Add 10 M NaOH to pH=5.5.

Hydroxylamine hydrochloride
Phenolphthalein

Standard zinc solution 0.01%. Dissolve 0.100gm of Zn metal in 1:1 Hcl and make up to 1 litre with water.

Sodium dithiodiethylcarbamate (NaDDC).
Add 100 gm diethanolamine to 90 gm CS₂ in distilling flask. Add cold NaOH solution (60 gm in 60 ml H₂O) dropwise to prevent rapid volatilization of CS₂, over a one hour period.

NOTE: With mixing over a four hour period, solution color changes from clear to yellow to orange as NaDDC precipitates.

Specified reagents give yield of 4 to 20 gm product, which is separated by centrifuging with ethanol (500 ml required). Two to three days drying time is necessary to convert excess NaOH to Na₂CO₃. (Excess NaOH in the zinc procedure would raise the pH.)

To test whether Cu reports for Zn with a new supply of NaDDC, /ml of 10 γ /ml Cu solution is added to a known Zn concentration. If absorbance does not increase beyond the Zn value, the Cu is complexed successfully.

APPENDIX D

Copper-Biquinoline Procedure

- Place 0.2 gm minus 100-mesh soil or rock sample in test tube.
- Add app. 1.0 gm of potassium pyrosulfate.
- Mix and fuse until reaction complete.
- Remove from flame and rotate tube so melt solidifies in thin layer on tube.
- Add 4 ml of 6N (1:1) HCl.
- Digest in water bath for 1 hour or until melt breaks up.
- Filter into 25 ml volumetric flask.
- Wash with hot water.
- Dilute to volume and mix. Store solution in refrigerator if estimation cannot be carried out within 1 hour after dilution.
- Transfer a 5 ml aliquot to a separatory flask.
- Add 50 mg hydroxylamine hydrochloride.
- Add 10 ml buffer solution
- Add 5 ml isoamyl alcohol-biquinoline solution with a glass buret.
- Stopper and shake vigorously for 1 minute.
- Allow solution to stand for 5 minutes.
- Drain and discard the inorganic phase.
- Insert absorbent cotton plug in the funnel stem.
- Drain organic solvent into absorption cell and determine absorbance at $546\text{ m}\mu$.

APPENDIX E

Zinc - Dithizone Procedure

- Dilute 5 ml of the solution prepared for Cu determination to 25 ml.
- To 5 ml of this solution in separatory flask add about 50 mg hydroxylamine hydrochloride. Swirl to dissolve.
- Add 1 drop phenolphthalein.
- Neutralize with 1:1 NH_4OH to first permanent pink.
- Add 10 ml buffer solution of pH = 5.5 and shake to dissolve precipitate.
- Add several mg of NaDDC and swirl to dissolve.
- Add 5 ml 0.001% W/V dithizone in CCl_4 .
- Shake vigorously for 2 minutes.
- Extract organic phase immediately through absorbent cotton into cell or test tube.
- Determine absorbance at 535 $\text{m}\mu$ without delay to avoid evaporation of CCl_4 , and decay of the dithizonate complex.

A fresh blank must be run for each day's procedure. Reagents must be dissolved before proceeding to further steps. Neutralizing with NH_4OH must be done carefully, drop by drop, as brown $\text{Fe}(\text{OH})_2$ precipitate may mask the pink color.

APPENDIX F

Notes on Spectrophotometer Operation

1. Beckman Model D.U.

- Turn selector switch to CHECK.
- Turn on tungsten lamp and current regulator to desired sensitivity.
- Rotate the Charge Adjust to zero the ammeter needle.
- Allow to warm up for 1 hour (preferably, two hours).
- Set a desired wavelength.
- Select desired phototube and load resistor.
- Insert standard and sample cells in holder and place in cell compartment.
- Position standard in light beam with positioning knob.
- Rotate dark current control to zero the null meter.
- Turn shutter on.
- Roughly zero the null meter by adjusting slit width.
- Accurately zero the null meter with the sensitivity control.
- Turn shutter off.
- Position sample in light beam.
- Turn selector switch to 1.0 or 0.1 if the transmittance is 10%.
- Turn shutter on.
- Zero the null meter with the transmittance control and note reading.
- Turn shutter off and position the next sample, repeat measuring procedure.

2. Bausch and Lomb 'Spectronic 20'

- Rotate wavelength control to obtain desired wavelength in millimicrons.
- Turn instrument on by rotating the zero control clockwise. When on, the jewel will glow.
- Allow 15 minutes warm-up time.
- Adjust zero control to bring meter needle to "0" on the percent transmittance scale.
- Insert test tube or cuvette containing standard in the sample holder. Use matched sets of test tubes, and set index line opposite index line on the sample holder.
- Close cover on sample holder.
- Rotate light control until meter reads "100" on the percent transmittance scale.
- Check "0" reading; check "100" reading.
- Insert unknown sample in place of the standard.
- Read percent transmittance or absorbance value directly from the meter, using mirror scale for accuracy.

- Turn light control counter clockwise before changing to another wavelength where the photocell might be more sensitive, to avoid burn-out of the meter.
- Use square cuvettes for utmost precision.
(Bausch and Lomb reference manual)

Comments

To minimize routine errors, repeat procedure for each sample until readings agree to within 0.2 per cent. Record the mean value.

Rinse test tubes and cuvettes with deionized water and dry in an oven. Use a standard potassium dichromate and sulfuric acid solution, when a stronger cleaning agent is required.

On either instrument, a reading is reproducible to within 0.2%T.

The Beckman instrument is advantageous in that:

1. Circuit fluctuations are smaller and less common.
2. Wavelengths in the ultraviolet and infra-red are available.
3. Burn-out of components through careless operation is less likely.

The Bausch and Lomb instrument is advantageous in that:

1. Warm-up time required is short.
2. It is more readily adapted to large-scale analysis. Several dozen samples in relatively inexpensive test tubes can be tested in succession, whereas the average analyst equipped with four expensive Beckman cells can only make three tests (plus blank) before washing and drying the cells.

Using test solutions prepared the previous day, the writer found he could test 15 samples for Cu and Zn using the B. and L., or 12 samples using the Beckman in a 12-hour day.

3. Steps in the manual procedure are few and simple in the relatively compact instrument.

4. One-half as much space is required. (12" x 16" vs. 7" x 55".)

APPENDIX G

Soil Profiles and Cu and Zn Data

These tables summarize Dr. A. R. Byers' field observations of soil profiles, and the writer's laboratory results.

The following abbreviations are used:

gry - grey
dk - dark
brn - brown
lim - limonitic
slt - silt/silty
cly - clay/clayey
sd - sand/sandy
dec - decomposed
gran - granular
plas - plastic
b - below
im.b.- immediately below
org. mtrl. - organic material
b.r. - bedrock
a.b. - above base
Bb - base of B horizon
Bt - top of B horizon
Bm - middle of B horizon
nut - nutty
frag - fragmental
par - parent

APPENDIX G

Soil Profiles and Cu and Zn Data

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
58+00S							
1+00W	C		2.5-3		29.3	11.2	2.6
3+00W	C		2.5-3	Lt gry slt, sd & lim			
3+25W	C		2.5-3	" " " " " "			
3+50W	C		2.5-3	Lt cly & lim			
3+75W	C		2.5-3	Dk cly & lim & org	61	8	7.6
59+00S							
2+00W	C		2-2.5	Gry slt cly			
2+50W	C		2-2.5	" " "			
3+00W	C	2-2.5	2-2.5	" " "			
3+00W	C		2-2.5	" " " & some lim			
3+25W	C		2-2.5	" " " " " "			
3+50W	C		2-2.5	" " "			
3+75W	C		2.5-3	Lt gry slt cly			
3+75W	C		4-4.5	Med. lt gry slt cly			
4+00W	C		2.5-3	" gry slt cly & org mtrl			
60+00S							
0+00W			2.5-1.0	on bedrock			
0+50W	Aob	1"		brn-bl, part dec			
"	A ₁	0.5"		gry brn, loose, gran			
"	A ₂	5"		lt gry plas nut cly			
"	B(?) _t	4"		med brn gry, plas nut cly			
"	C		30"b. A _o	indistinguishable from B	20.2	5	4
1+00W	Aob	2"		(on road-contam?) -brn-blk part dec			
"	A	1"		gry brn, loose gran			
"	B _m	12"	4"b. A _o	gry brn nut cly			
"	B _b						
"	C		28"b. A _o	lt gry brn sd dk brn blk, slightly dec	28.8	4.1	7.0
1+50W	Aob	2"					
"	A	0.5"	4"b. A _o	gry loose gran			
"	B _t	14"	12"b. A _o	gry nut cly			
"	B _b						
"	C		28"b. A _o	gry brn gran cly	19.0	3.3	5.8

Appendix G

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
60+00S							
2+00W	A _{ob}	2"		brn blk, part dec, no lime			
"	A	0.5"		gry brn, gran, loose no lime			
"	B	14"	4"b. A _o	brn stiff fine nut cly			
"	B _o						
"	C	7.5"	20"b. A _o	lt gry brn slt cly - high lime - b.r. at 24"	18.0	3.5	5.2
2+25W	C		2-2.5		78.3	5.7	13.7
2+50W	A _{ob}	3"		blk, slight dec. no lime			
2+50W	A	1.5"		gry brn gran, rootlets no lime			
"	B	8"	4"b. A _o	brn slt cly			
"	C		28"b. A _o	lt brn slt cly, lim no lime			
2+75W			2-2.5		30.5	4.3	7.1
3+00W	A _o (?)	10"	6" b.s.	blk under top 2"; rest=part dec, loamy			
"		3"		lt gry cly, some lim			
"		3"		dk gry org loam			
"				med gry cly			
"	C		2-2.5		12.0	1.3	9.3
3+25W	C		2-2.5		20.3	10.6	1.9
3+50W	C		2-2.5	gry plas cly (org mtrl=top 20")	13.3	8.9	1.5
3+75W	C		2.5-3	gry plas cly	44.8	4.0	11.2
4+00W	C		2.7-3	gry plas cly (org mtrl=top 29")	16.4	9.6	1.7
4+25W	C		2.7-3	dk gry; surface- type muck	552.	10	55.2
61+00S							
0+00W	A _o	1.5"		dk brn blk, part dec			
	A			brn gran loose			
	C		2-2.5	lt gry brn sd			
0+50W	A _{ob}	1"		dk brn, part ded			
"	A(?)	0.5"	im.b. A _o	gry brn lumpy slt cly			
"	B(?)		6"b. A _o	gry brn nut cly, hard (c=slt cly)			
1+00W	A _o	1"		dk brn, largely dec			
"	A(?)	3"	im.b. A _o	gry brn hard cly			
"	B(?)		6"b. A _o	gry brn nut to blocky cly (c=brn-cly slt)			

Appendix G

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
61+00S							
1+50W	A ₀	1"		brn part dec			
"	A	5"	im.b.	1" gry brn; 4" lt gry			
"	B		A ₀	brn gran cly			
			6"b.	gry brn nut cly (c=			
			A ₀	gry brn cly)			
2+00W	A ₀ b	3"		moss, part dec mtrl			
"		1"	im.b	org mtrl			
"		2"	A ₀				
			6"b.	dk brn sd (c=gry			
			A ₀	brn, to lim clay)			
3+00W	A ₀ b	1"		dk brn, part dec			
"	A?	1"	im.b.	gry brn sd			
"			A ₀				
	B?	20"	6"b.	brn sd, lim patches			
			A ₀	(c=cly slt)			
3+50W	A ₀ b	4"		dk brn, part dec			
"	A	3"	im.b.	lt gry sd			
"			A ₀				
	B		4"b.	choc.brn sd (c=			
			A ₀	lim cly sd)			
4+00W				gry brn sd cly and cly			
				sd, lim			
0+50E	C		18"	gry brn, sd, on b.r.			
				(A=1.5" part dec;			
				A= lt gry)			
1+00E	C		26"	lt gry slt cly, on b.r.			
				(A ₀ =dk, part dec;			
				A=brn)			
1+50E	C		30"	lt gry slt (A ₀ =2" blk,			
				part dec; A=gry brn			
				slt)			
2+50E	C		26"-	gry cly (A ₀ =4" blk,			
			30"	part dec; A=gry,slt)			
61+90S							
3+25W	C		26"	brn gry cly sd to			
			b.s.	slt cly			
62+00S							
0+00W	C		2-2.5		31.1	1.2	25.9
"			12"b.	lt brn gry sd	28.6	6.0	4.8
"			A ₀				
"			16"b.	lt gry cly sd	45.7	1.4	32.6
"			A ₀				
"			22"-	med brn gry sd	24.6	1.3	19.0
"			26"b.				
"			A ₀	" " " "			
"			30"b.				
"			A ₀				

Appendix G

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
62+00S							
0+50W	C		2-2.5	med gry clay	29.4	1.1	26.8
1+00W	C		2-2.5	lt gry brn cly	32.2	5.5	5.9
1+50W	C		2-2.5	stiff gry cly	39.7	8.5	4.7
1+75W	C		2-2.5		34.2	9.2	3.7
2+00W	C		2-2.5	med gry brn hard cly	20.7	13.2	1.6
2+00W	C		2-2.5		22	12.7	1.7
2+25W	C		2-2.5		28	3.0	9.3
2+75W	C		2-2.5		29.3	3.8	7.7
3+00W	C		2-2.5		23.5	8.7	2.7
3+25W	C		2-2.5		112.5	4.0	29.1
3+50W	C		2-2.5	Offset 23'N	26.8	1.2	22.4
3+75W	C		2-2.5	fine lt gry brn (lim) sd	64.3	5.5	11.7
4+00W	C		2-2.5		36.4	6.7	5.4
"			20-25"	gry brn sd	31.8	3.2	10
"			25-28"	slt gry cly	49.4	5.0	10
"			28-33"	gry brn sd, lim nodules, weath.bio.	64.1	6.6	9.7
4+25W	A _o	9"	2"a.b.	dk brn blk; irreg base; boulders (old beach)	67.0	8.6	7.8
"			i.b.	gry gran sd	46.7	2.5	18.7
"			A _o				
"			2"b.	gry slt mtrl	9.1	0.9	10.1
"			A _o				
"			5"b.	lt gry mottled to lim brn	66	4	16.5
"			A _o				
"			12"	ditto; at water seep	23.8	4.4	5.4
"			b.A _o				
"	C		2-2.5	lim sd	25.1	5.7	4.4
4+50W	A _{ob}	8"		dk brn blk peaty	38.4	1.8	21.3
"		3"	im.b.	gry grn sd slt			
"			A _o	(org)	57.0	1.8	31.7
"		9"	9"b.	mottled gry gran to brn lim sd	16.6	1.2	14.3
"			A _o				
"			12"b.	gry cly below lim sd	16.3	4.2	3.9
"			A _o				
"	C		2-2.5		31.5	7.5	4.2
4+75W	C		2-2.5	gry cly	31.5	6.1	5.2
0+50E	C		24-				
			28"	brn sd cly	78.0	5.9	13.2
1+00E	C		26-	lt gry brn cly slt	35.9	0.6	60.0
			30"				
1+50E	C		24-	lt gry cly slt	43.6	5.7	7.7
			28"				

Appendix G

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
62+15S							
2+77W	A _o	2.5"		dk brn blk org mtrl	22.4	3.5	6.4
"	A	3.5"		lt brn gry, hor lay, brittle	36.6	7.8	4.7
"	B _t	8"		med gry angular pellets	5	5.9	0.84
"	B _b		5"b.		10.4	3.7	2.8
"	C		B _t 6"b. B	lt med brn boulder cly (parent mtrl)	18.8	3.3	5.7
63+00S							
0+00W	A _{ob}	2"		brn-bl, undec	1047.0	43.0	24.4
"	A ₁	0.5"		brn gran cly	61.3	7.9	7.7
"	A _{2m}	5"		lt gry brn nut cly (grad with B)	60.0	5.4	11.1
"	B _t	6"		med gry brn nut cly	17.7	3.0	5.9
"	C		2-2.5	gry slt cly	12.8	2.8	4.6
0+50W	A _o	1.5"		dk brn, part dec	147.0	10.4	14.2
"	A(?)	2"	im.b.	lt gry brn gran cly	30.5	5.2	5.9
"	B(?)		A _o 4"b.	med gry brn nut to blocky cly	69.5	8.7	8.0
"	C		A _o 2-2.5	gry brn cly sd (disturbed) dk brn, part dec	43.4	7.3	6.0
1+00W	A _o	1"			380.0	39.8	9.6
"	A(?)	2"	im.b.	gry brn gran to fragmental hard cly	38.6	5.1	7.6
"	B(?)		A _o 5"b.	gry brn hard nut cly	7.1	8.8	0.8
"	C		A _o 2-2.5	gry brn slt cly	44.1	11.8	3.7
1+25W	C		2-2.5	cly	20.2	6.5	3.1
1+50W	A _o	2"		brn, part dec	1030	79.5	13.0
"	A(?)	1"	im.b.	gry brn loose gran cly	30.5	5.1	7.6
"	B(?)		A _o 6"b.	gry brn soft frag cly	25.2	6.9	3.7
"	C		A _o 2-2.5	gry brn stiff cly	27.5	7.5	3.7
1+75W	C		2-2.5	cly	41.2	7.1	5.8
2+00W	A _o	1"		brn, part dec	174.0	24.6	7.1
"	A(?)	1"	im.b.	brn gry bl loose grn cly	62.2	6.2	10.0
"	B(?)		A _o 6"b.	lt gry brn nut cly	10.2	6.1	1.7
"	C		A _o 2-2.5	med gry brn stiff cly	7.6	11.5	0.7
2+25W	C		2-2.5	cly	10.2	7.3	1.4
2+50W	A _o	2"		brn bl, part dec	58.6	4.6	12.7

Appendix G

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
63+00S							
2+50W	A ₁ (?)	1.5"	im.b. A ₀	lt gry gran cly			
"	A ₂ (?)	4.5"		lt gry brn hard cly			
"	B(?)		7"b. A ₀	lt gry brn nut cly	8.1	7.2	1.1
"	C		2-2.5	lt gry brn slt cly	30.1	6.2	4.9
2+75W	C		0.5-1	5.0' w. of outcrop	50.4	7.1	7.1
3+00W	C		2.0	pit side on bedrock	24.3	3.3	7.4
3+25W	A ₀	1.5"		dk brn, undec org mtrl	1157.0	58.3	19.8
"	A ₁	1"		brn, loose, rootlets	38.0	5.1	7.5
"	A _{2m}	9"		gry nut cly, irreg. base	39.2	3.6	10.9
"	B _t	12"		brn, slt, lim streaks	8.7	4.7	1.9
"	C		2.5-3	lt gry brn slt cly - pit side, 1' above b.r.	57.0	2.0	28.5
3+50W	A _{0b}	2"			372.0	52.0	7.2
"	A ₁	1"			365.0	31.0	11.8
"	A _{2m}	10"		gry cly, nut, hard	44.7	5.4	8.3
"	B _t				10.6	5.0	2.1
"	C		2-2.5	yellow gry slt, fine sd	34.4	6.8	5.1
3+75W	A _{0b}	2.5"		part dec. brn with bl at base	358.0	26.5	13.5
"	A ₁	1"		gry brn, gran, rootlets	38.2	5.8	6.6
"	A _{2m}	9"		gry clay, nut,	61.0	1.0	61.0
"	B _t			gry brn, slt, structure less	55.5	5.2	10.7
"	C		2-2.5	sd, lt gry	40.5	3.9	10.4
4+00W	A ₀			brn bl, part dec	103.0	5.3	19.5
"	A ₁ (?)		3"b. A ₀	slt cly	46.5	1.1	42.2
"	B _t			cly?	35.0	-	-
"	B	8"	12"b. A ₀	lt gry brn cly - some rootlets	30.0	2.4	12.5
"	C		2.5-3	lt gry grn slt cly, lim, sericite	49.3	4.3	11.4
4+25W	A ₀			brn blk part dec (A absent)	66.30	80.0	8.3
"	B _t	8"		lt gry cly - some rootlets	105.2	6.2	17.0
"	C _t			lt yellow gry cly (lim stain)	68.8	3.7	18.6
"	C			lt gry brn slt cly	76.1	4.7	16.2
4+50W	A _{0b}	5"		dk brn undec; thin bl layer at base	160.0	7.9	20.2

Appendix G

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
63+00S							
4+50W		5"	2"b. A ₀	med gry, cly slt, no lime	52.8	3.8	13.9
"		12"	12"b. A ₀	lt gry slt sd limey	131.5	4.3	30.6
"	C		2-2.5	lt brn slt sd limey	56.8	7.5	13.2
4+75W	C		2-2.5	lt gry grn slt cly lim, sericite	29.3	4.9	6.0
5+00W	C		1"b. A ₀	1st sand, gry	39.8	4.0	10.0
"			7"b. A ₀	blk org mtrl (flooded forest)	131.0	14.0	9.4
"			10"b. A ₀	2nd sand gry	47	4.3	10.9
"	C		2-2.5	gry boulder clay brn-bl, mostly undec	23.5	4.9	4.8
0+50E	A _{0b}	1.5"			235	20	11.7
"	A ₁	0.5"		gry gran cly			
"	A _{2m}	6"		gry nut cly	34	4.3	7.9
"	B _t	3"		lt gry brn nut cly	16.8	5.5	3.1
"	C		26- 30"	gry brn gran plus cly	23.3	8	2.9
1+00E	C		"	lt gry grn plus clay	12	6.3	1.9
1+50E	C		"	dk gry grn plus clay (top 21"=org mtrl)	16.4	9.3	1.8
4+50E	C		"	gry brn s. cly	22.8	0.6	38.0
5+00E	C		25- 32"	yellow gry sd	22.4	4.2	5.4
5+50E	C		"	lt gry brn cly sd	16.0	2.2	7.3
6+00E	C		"	" " " " "	26.6	4.4	6.1
6+50E	C		24- 28"	" " " " "	50.9	6	8.5
7+00E	C		26- 32"	" " " " "	40.5	7	5.8
7+50E	C		"	" " " " "	39.3	3.7	10.6
8+00E	C		"	gry brn stiff cly	10.1	8.2	1.2
63+50S							
3+00W	C		2-2.5		32.8	6.9	4.8
3+25W	A _{0b}	3"		dk brn, with thin bl layer at base; part dec			
3+25W	A ₁	0.5"		brn, gran			
"	A _{2m}	7"		gry hard cly	43	6.4	6.7
"	B _t (?)			gry cly			
3+50W	A ₀	2"		dk brn-bl, part dec			
"	A ₁	1"		dk gry, gran sd			
"	A _{2m}	10"		lt gry, sd			
"	B _t (?)			med gry brn sd, grad with A ₂			

Appendix G

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
63+50S							
3+75W	A ₂	12"		non-lim gry cly			
4+00W	A _{2m}	6"		hard gry cly			
"	B _m	5"		gry brn slt cly			
4+25W	A _{ob}	2"		brn bl, part dec			
"	A _{1t}	2"		gry, loose, gran, root- lets			
"	A _{2m}	4-6"		gry cly, rough $\frac{1}{2}$ " nodules			
"	B _m	2-4"		gry brn cly, irreg. (C=gry slt cly)			
64+00S							
0+00W	C		2-2.5		49.3	6.6	7.5
0+50W	A _{ob}	3"		dk brn blk, part dec	858.0	20.0	42.9
"	A ₁ (?)	4"	imbb.	med gry brn stiff nut cly	97.0	7.0	13.8
"	B(?)		5"b.	lt gry brn stiff			
"			A _o	blocky cly	21.0	6.7	3.1
"	C		2-2.5	gry brn stiff cly	76.0	9.5	8.0
1+00W	C		2-2.5		77.0	6.9	11.2
1+25W	C		2-2.5		43.8	7.1	6.2
1+50W	C		2-2.5	cly	62.5	10.4	6.0
1+75W	C		2-2.5	lt gry cly	58.8	4.2	14.0
2+00W	A _{ob}	2.5"		bl part dec (contam. by tin cans?)	116.0	12.2	9.5
"	A ₁	0.5"		gry bly, gran but plas	59.3	5.7	10.4
"	A _{2m}	8"		lt gry cly, plas, nut	89.3	8.5	10.5
"	B-C _b			med gry brn gran cly	47.0	7.3	6.5
"	C		2-2.5	indistinguishable from B	30.8	8.3	3.7
2+25W	C		2-2.5		45.3	6.3	7.2
2+50W	A _{ob}	2.5"		dk brn bl, part dec	195.0	9.6	20.4
"	A ₁	1"		med gry, loose, gran	72.1	8.6	8.4
"	A _{2b}	9"		lt gry, compact cly, nut	80.1	8.5	9.4
"	B-C _b			med gry gran cly	75.5	11.8	6.4
"	C		2-2.5	indistinguishable from B	53.3	10.4	5.1
2+75W	C		2-2.5		70.5	7.6	9.3
3+00W	A _{ob}	2.5"		bl part dec	215	20.6	10.4
"	A ₁	0.5"		gry sd cly	86.5	8.8	9.9
"	A _{2m}	11"		lt gry cly, plas, frag	51.2	6.9	7.4
"	B _t (?)			med gry cly, plas; grad with C,	40.8	6.2	6.6
"	C		2-2.5	if disting. at all	75.0	8.3	9

Appendix G

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
64+00S							
3+25W	A ₀	2"		org mtrl, bl, part dec	210	15.3	23.7
"	A ₁	1½"			98.8	9.4	10.5
"	B _t	11"			35.1	8.1	4.3
"	B		6"-9"		35.3	9.3	3.8
"			b.B _t				
"	C		2-2.5	gry cly	33.2	7.0	4.8
3+50W	C		2-2.5	gry brn cly	61.2	7.0	8.74
3+60W	A ₀	3"		org mtrl	1725	28.4	60.8
"	A ₁	1"			808	7.8	103.8
"	B _t				54	3.9	13.8
"			7"-10"		449	6.8	66.0
"			b.B _t				
"	C		20-23"	parent mtrl	124	9.5	13.1
3+75W	C		1.7-2'	br gry slt sd; gravel	2592	15.2	170.0
4+00W	C		2-2.5	lim gravel; malachite and azurite	3335	21.6	154.0
4+25W	A ₀	1"		slt sd (probable old beach)	91.4	5.3	17.2
"	A	1"		gry sd	183.0	6.0	30.6
"	B	6"	4"	brn cly	99.0	2.6	38.1
"	B _b		8"	gry cly	11.1	4.1	2.7
"	C		2-2.5'	malachite sand	4965	9.3	535.9
4+50W	A ₀	7"		brn-blk, undec	349	51.5	6.8
"		2"		dk brn	64.7	6.1	10.6
"	B _t				62.5	4.6	13.6
"	B		7"b.	brn gry slt cly grad. to par. mtrl	47.6	3.3	14.4
"	B(?)		12"b.				
"			A ₀		56.0	3.7	15.6
"	C		2-2.5	slt sand (par. mtrl)	44.0	2.6	16.9
4+75W	A ₀	6"		bl; undec (A absent)	200	3.3	60.6
"	B	12"	im.b.		22.6	3.9	5.8
"			A ₀				
"	B		12"b.				
"			A ₀		28.0	4.8	5.8
"	C		2.5'	par mtrl	50.5	5.9	8.6
5+00W	C		2-2.5'		59.4	6.6	9.0
0+50E	C		2.5		53.9	13.6	4.0
1+00E	C	2-2.5			39.9	7.6	5.3
1+50E	A ₀		2.5	org muck	2930	32	91.5
64+15S							
1+00W	A _{0b}	2"		bl part dec	90.5	5.7	15.9
"	A ₁	1"		gry brn, loose, gran	67	0.9	74.5
"	A _{2m}	8"		lt gry cly	29.8	6.1	4.9
"	B-C _t			med gry gran cly	43.8	8.3	5.3

Appendix G

Station	Hor.	Thick	Depth	Description	Cu ppm	Zn ppm	Cu/Zn
64+25S							
1+50W	Aob	2"		bl part decomp	75.9	12.4	6.1
"	A1	1"		gry, cly, gran but plas	8.4	8.4	1.0
"	A2m	8"		lt gry, cly, nut ($\frac{1}{2}$ ")	0	5.1	0
"	B-Ct			med gry brn cly, gran (indist. from C)	61.0	8.3	7.4
64+50S							
3+00W	C						
3+25W	C			lt gry cly			
3+50W	C			" " "			
3+75W	C			" " "			
4+00W	C			" " " - some lim			
4+25W	C			" " " " "			
4+50W	C			" " " " "			
4+75W	C		2-2.5	" " " " "			
5+00W	C		2.5-3	" " " " "			
65+00S							
0+00W	C		1-1.5	Yellow-brn slt sd - on b.r.	13.6	3.9	3.5
1+00W	C		2-2.5	gry cly	40.0	6.5	6.2
1+25W	C		"	" "	49.0	6.0	8.2
1+50W	C		"	" "	48.6	5.7	8.5
1+75W	C		"	" "	15.1	7.9	1.9
2+00W	C		"	" "	53.5	10.0	5.4
2+50W	C		"	" "	51.8	9.0	5.8
2+75W	C		"	" "	31.4	7.2	4.4
3+00W	C		"	" "	26.2	7.9	3.3
3+25W	C		"	" "	9.3	5.7	1.6
3+50W	C		"	" "	34.2	4.5	7.6
4+00W	C		"	" " 0-2.0 = A ₀	42.5	5.9	7.2
4+25W	C		"	" " 0-2.0 = A ₀	11.1	11.8	0.94
4+50W	C		"	" " 0-2.0 = A ₀	20.9	5.0	4.2
4+75W	C		2.3- 2.5	" "	2.5	3.0	0.8
5+00W					315.0	9.2	34.2
5+25W				0-2.3=A ₀	40.2	10.9	3.7
66+00S							
1+00W	C		2-2.5	slt, lim			
1+50W	C		"	slt sd			
2+00W	C		"	lt gry cly			
2+50W	C		"	" " "			
3+00W	C		"	" " "			
3+25W	C		"	" " "			
3+75W	C		2.5-3	" " "			
4+00W	C		"	" " "			
4+25W	C		"	" " " , lim			
4+50W	C		"	" " " "	51.4	10	5.1