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BOTANY IN RELATION TO SUB SURFACE GEOLOGY

BY

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ABSTRACT

Agriculturists have long been interested in the minor element content of trees and lesser plants and of the soils in which they grow. This paper deals with the relation of plants to ore deposits. The investigations indicate that the zinc and copper content of some trees and lesser plants may reflect, to a striking extent, the presence of zinc and copper concentrations in the underlying soils or rock formations.

INTRODUCTION.

Investigations into the role of botany in relation to sub-surface geology were commenced at the University of British Columbia in 1945. The objective was to see if vegetation could be used to indicate the presence of sub surface ore bodies. The credit for starting this work in British Columbia actually belongs to Mr. and Mrs. Dorbill who, through Professor Gage, chairman of The Committee on Prizes and Scholarships, offered the University a prize to be known as the Dorothy and William Dorbill Essay Prize in Botany and Geology. With the additional aid of a Special Research Grant for Botany and Sub-surface Geology, made available by the Board of Governors of the University of British Columbia, field work commenced in the spring of 1945, under the direction of Dr. H.V. Warren.

After consultation with the Departments of Botany and Agronomy, Mr. J.W. Warden, a qualified and experienced botanist, was engaged to collect from two hundred to two hundred and fifty plant samples from various mining districts. These districts were selected as being districts where it would be possible to select plants from some areas known to be underlain by ore bodies and from other areas known to be barren of mineralization. Mr. Warden, aided by individuals familiar with the local geology, collected samples during the spring and summer of 1945. During the winter of 1945-46 Mr. R.N. Williams undertook the task of analyzing the samples

for copper and zinc.

SUMMARY OF SOME OF THE WORK DONE IN THE FIELD OF
BOTANY AND TRACE ELEMENTS

Much work has been done by agronomists, horticulturists and botanists on the occurrence of "trace" elements in soils and plants. As yet little has been published correlating the amounts of these "trace" elements in soils and plants with the underlying geological formations. It may be that generally there is no direct correlation, but in some cases it can be shown that the mineral content of soils and plants is determined by the mineral content of the parent rock. The more important "trace" or "minor" elements are considered in agriculture and botany to be, Aluminum, Boron, Calcium, Cobalt, Copper, Sodium, Manganese, Magnesium, Molybdenum, Silica, and Zinc. It is known that some of the above elements plus others, are essential for the growth of plants and animals, but their functions in growth are not agreed upon.

The following few examples will show how important these "minor" elements are to plant and animal growth. Zinc compounds applied to soils prevent "frenching" on citrus fruits, rosetting on pecan and apples, "little leaf" on peach and grape-vine and "yellows" on walnut. (2). Copper deficiencies in pastures and consequently in animals is constantly associated with "falling disease" in the cattle of the south western part of Western Australia. (3) The "Grand Traverse" or "Lake Shore" disease in Michigan cattle is essentially due to cobalt deficiencies; (4) "Pining" in sheep has been

corrected by the administration of cobalt and cobalt-rich fertilizers to the pasture soils (5). Some English herbage containing a large amount of molybdenum, when fed to cattle causes a failure of milk, loss of condition and even death (6).

It has been known for some time that some certain plants will indicate the presence of concentrations of certain elements in the soil. Heckel (7), in 1899 stated that Polycarpaea spirostylus (Pink Family) so frequently contains copper, that in Australia, its growth is considered to be an indication of copper in the soil. Viola calaminaria (Violet Family) similarly indicates the presence of zinc. Bateman (8) found that Rosa Woodsi (wild rose), Equisetum variegatum (horsetail) and Dasiphora fruticosa (Bush cinquefoil) thrived in a copper tailing region, while willow, alfalfa and red clover had been killed by the increased mineral concentration. The plants growing in the copper-rich region contained from 62 - 6210 parts per million of copper, while willow, red clover and grasses growing in a non copper-rich area of the same vicinity contained no copper. Bateman concludes, that because some plants were unable to adjust themselves to the new environment while other plants flourished, a decided selective ability is indicated. Prat and Komarek, (9) investigating the mineral content of plants found that in soils containing 1 - 33% copper, the species Agrostis alba (red top grass) and Melandrium silvestre (Pink Family), contains 0.2 - 3.25% copper in their ash.

The mineral content of plants varies with the species and with the organs of the individual plants. Gamelin (10) investigated 57 trees and seven shrubs of the order Pinales (pines) of Quebec. He found that the manganese concentration varied inversely with the iron. The investigations revealed that the highest manganese content was in the leaves, then in the bark, twigs, heart wood, fruits and sapwood. Black spruce and tamarack contained the most manganese and white cedar the least. Robinson (11) has found the leaves from hickory trees growing on soils derived from granite and gneiss, contained more rare earths than did leaves from other species growing on the same soils; and more than leaves from hickory trees growing on other soils.

The mineral concentration of the leaves of the various species changes during the growing season. McHargue and Roy (12) found that the copper and zinc content of leaves increased with age and Robinson (11) found that mature hickory leaves have a higher rare earth content than the young leaves. It was thought that the mineral content of the leaves might migrate to the branches during the autumn, but ter Meulen (13) has shown that in the case of molybdenum there is no such migration. It is probable that this fact holds true for the other elements.

The composition of the parent material has a varying influence on the mineral content of a soil depending on the conditions existing during soil formation. According to

Holmes (2), under acid conditions there would be less copper and zinc held in the soil than under basic conditions. Robinson (14) found that the Desert, Chernosem, and Prairie soils are usually high in boron, while soils of the Coastal Plains and Podsol soils are low in boron. The difference in boron content may be due to an uneven distribution of boron in the parent geological formations. The evidence from Robinson's analysis shows that the difference between the soils represents primary minerals, tourmaline in particular in the parent rock, although the evidence presented does not exclude the formation of an acid insoluble secondary compound.

Plants have been used extensively in the U.S.A. as indicators of seleniferous soils. These indicators are defined as plants which contain significant amounts of selenium during all or a major part of their annual growth and thrive only in its presence (15). The main indicators are all species of Stanleya (Princesplume), Oenopsis, (Goldenweed) and Xylorrhiza (aster). In South Dakota, the Niobrara formation and soils derived from it, is most consistently seleniferous. The lower Sharon Springs members of the Pierre (shale) formation is consistently high in selenium, but this formation resists weathering, seldom forms soils, and vegetation is seldom found growing on it. Further studies (16) are believed to demonstrate that numerous geological formations from the late Paleozoic to Quarternary can support native seleniferous plants, which are found rooted in both igneous and sedimentary

rocks including monzonite, limestone and shale.

From the above examples it can be seen that in many cases there is a relationship between the mineral content of the plants, soils and parent rock. Goldschmidt (20) noted a relationship as the following quotation will show.

"When the investigation is extended to cover a whole forest one may recognize local differences in the composition of the sub soil by noting differences of rare elements in the leaves of various trees. ----- It has, however, been shown by experiments carried out in Sweden and Finland, that ore deposits are in many cases indicated by a positive test on the ashes from the leaves of trees."

RESULTS OF THE PRELIMINARY INVESTIGATIONS

The scope of these investigations has been limited, at present, to the quantities of copper and zinc present in various plants. The detailed results given later in this report will show that there is a relationship between the quantities of these two elements in plants and the quantities of these two elements in the material surrounding the plant roots.

One of the main problems in this research was the obtaining of satisfactory control samples (1). During the collecting of the first set of samples the only consideration taken into account was the probable occurrence of copper and zinc, either in the ground water, or in the soil, or in the sub-surface rock in greater concentration than would normally be found in non-mineralized areas. Note was made of the pH

of the soil, drainage conditions, or the age of the plant from which the samples were taken.

The results can be summarized as follows:

1. Copper and zinc play different roles in plant growth. The exact function of each element is not definitely known.
2. Cones and needles of conifers, or fruits and leaves of deciduous trees offer possibilities for the detection of unusual concentrations of copper and zinc.
3. The woody parts of plants seem to vary less widely in copper and zinc content than the leaves or seed.
4. The copper and zinc content of plants growing in the same vicinity varies widely between species.

DETAILED RESULTS

The following tables give the detailed results of some of the more representative samples. The term positive area is used to indicate an area in which there was thought to be, by local geologists, an unusual amount of copper or zinc. Correspondingly a negative area connotes an area devoid of any unusual concentration of either of these two elements.

BRITANNIA: As representative of a copper rich area

Samples were obtained from this camp after a careful choice of positive and negative areas had been made by W.T. Irvine, geologist for the Britannia Mining and Smelting Co.

The following tables show the copper and zinc content of some corresponding "positive" and "negative" samples.

TABLE 1. COPPER - BRITANNIA

BOTANICAL NAME	COMMON NAME	POSITIVE AREA		NEGATIVE AREA	
		Sample No.	Copper in p.p.m. of ash	Sample No.	Copper in p.p.m. of ash
Tsuga Mertensiana	Mountain Hemlock (Cones)	205	34,560	212	1,540
Tsuga Mertensiana	Mountain Hemlock (Bark)	206	2,060	213	210
Abies amabilis	Amabilis Fir (Leaves)	221	1,400	215	430
Vaccinium ovalifolium	Blueberry (Leaves)	217	2,000	227	570
Alnus rubra	Alder (Leaves)	223	25,650	230	310
Echinopanax horridos	Devil's Club (Leaves)	225	12,810	228	290
Average Copper in p.p.m.			13,080		558

TABLE 11 ZINC - BRITANNIA

BOTANICAL NAME	COMMON NAME	POSITIVE AREA		NEGATIVE AREA	
		Sample No.	Zinc in p.p.m. of ash	Sample No.	Zinc in p.p.m. of ash
Tsuga Mertensiana	Mountain Hemlock (Cones)	205	220	212	1,920
Vaccinium ovalifolium	Blueberry (Leaves)	217	500	227	470
Alnus rubra	Alder (Leaves)	223	2,560	230	490
Average in p.p.m. of ash			1,093		960

The examples cited in tables 1 and 2 are representative of most of the samples analyzed. It can readily be seen, from Table 1, that different species growing in the same vicinity contain different amounts of copper, and that the different organs of the same species also contain different amounts of copper. In a copper rich area most of the samples from a positive area contain more copper than corresponding samples from a negative area, while there seems to be no such correlation possible with reference to zinc.

CHAPMAN CAMP: Representative of a zinc rich area.

The samples from this camp were selected after a discussion of the problem with H.R. Banks, Superintendent of the Sullivan Concentrator and Dr. C.O. Swanson, Geologist for the Consolidated Mining and Smelting Company Ltd. In this area it may be better to think of the samples from positive areas as being reasonably safe, but those from the negative areas are by no means satisfactory.

TABLE III ZINC - CHAPMAN CAMP

BOTANICAL NAME	COMMON NAME	POSITIVE AREA		NEGATIVE AREA	
		Sample No.	Zinc in p.p.m. of ash	Sample No.	Zinc in p.p.m. of ash
Pinus contorta	Lodgepole pine (Cones)	152	19,780	175	6,750
Pinus contorta	Lodgepole pine (Bark)	153	2,780	174	1,960
Salix Hookeriana	Willow (Bark)	161	490	179	40
Larix occidentalis	Larch (Leaves)	150	2,540	168	2,390
Larix occidentalis	Larch (Bark)	148	2,690	166	1,130
Populus tremuloides	Aspen (Leaves)	147	4,000	182	1,640
Shepherdia canadensis	Soopolallie (Leaves)	163	1,090	167	740

Average Zinc Content in p.p.m. positive 4,767
negative 2,093

10

TABLE IV COPPER - CHAPMAN CAMP

BOTANICAL NAME	COMMON NAME	POSITIVE AREA		NEGATIVE AREA	
		Sample No.	Copper in p.p.m. of ash	Sample No.	Copper in p.p.m. of ash
Pinus contorta	Lodgepole pine (Cones)	152	210	175	1,000
Pinus contorta	Lodgepole pine (Bark)	153	260	174	930
Populus trichocarpa	Black Cottonwood (Leaves)	155	190	180	320
Larix occidentalis	Larch (Leaves)	150	60	168	340
Larix occidentalis	Larch (Bark)	148	380	166	130
Populus tremuloides	Aspen (Leaves)	147	220	182	290
Shepherdia canadensis	Soopolallie (Leaves)	163	120	167	130

Average Copper Content in p.p.m. Positive 205 negative 448

TEXADA ISLAND: As representative of a copper rich area

Satisfactory samples were difficult to obtain from this camp. As mineralized outcrops are rare and small the samples were taken from the vicinity of old mine dumps. These deposits are replacements in limestone and with the presence of so much basic material there is far less chance of copper being dissolved in ground water than there would be say at Britannia, where the ground waters would be more acidic. The negative samples were taken adjacent to the top of a limestone quarry where extensive operations had shown no signs of copper. Mr. C. Cox, Manager of the Little Billy Mine kindly assisted in choosing the places best suited for making collections.

TABLE \bar{V}

BOTANICAL NAME	COMMON NAME	POSITIVE AREA		NEGATIVE AREA	
		Sample No.	Copper in p.p.m. of ash	Sample No.	Copper in p.p.m. of ash
<i>Pseudotsoga taxifolia</i>	Douglas Fir (Cones)	2	10,310	18	370
	(Bark)	6	930	19	360
	(Leaves)	1	250	17	50
	(Wood)	3	3,210	20	1,200
<i>Thuja plicata</i>	Western Red (Leaves)	4	540	21	270
	Cedar				
<i>Tsuga heterophylla</i>	Western Hemlock (Bark)	15	360	25	910
	(Leaves)	14	290	24	490
<i>Pteris aquilina</i>	Bracken (Average of No	10)			
		11)	1,110	28	250
		12)			

TABLE VI

BOTANICAL NAME	COMMON NAME	POSITIVE AREA		NEGATIVE AREA	
		Sample No.	Zinc in p.p.m. of ash	Sample No.	Zinc in p.p.m. of ash
Pseudotsuga taxifolia	Douglas Fir (Leaves)	1	320	17	600
Thuja plicata	Western Red (Leaves)	4	270	21	400
	Cedar (Wood)	9	580	23	4,800
Tsuga heterophylla	Western Hemlock (Bark)	15	1,040	25	490
	(Leaves)	14	60	24	270

Average Zinc Content in p.p.m.	positive	454
	negative	1,312

TABLE VII AVERAGE COPPER CONTENT OF SAMPLES

	<u>POSITIVE AREA</u>	<u>NEGATIVE AREA</u>
FROM: Britannia	13,080 p.p.m. of ash	558 p.p.m. of ash
Chapman Camp	205 " " "	448 " " "
Texada Island	2,002 " " "	487 " " "

From the above table it would seem that the average copper content of plants growing in non-mineralized areas varies between 50 and 500 p.p.m. of ash. The low average of samples from the positive area at Chapman Camp may be due to the fact that plants having a high concentration of zinc do not need or cannot absorb as much copper as plants growing under normal conditions.

TABLE VIII AVERAGE ZINC CONTENT OF SAMPLES

	<u>POSITIVE AREA</u>	<u>NEGATIVE AREA</u>
FROM: Britannia	1,093	960
Chapman Camp	4,767	2,093
Texada Island	454	1,312

The zinc content of plants seems to vary less widely than the copper content. In most cases plants seem to contain more zinc than copper, the ratio being one part of copper to two of zinc. The averages for Texada Island are generally lower than those from the other camps. This may be explained by the less acidic conditions prevailing in the area due to

the abundance of limestone.

The above results may be misleading when compared to the results reported later in the paper. Tables 1 - 8 report the copper and zinc as parts per million of ash, while the later results are given as parts per million of dry plant material. Table 9 gives the results of table 7 & 8 expressed as parts per million of dry plant material.

TABLE IX

AVERAGE COPPER AND ZINC CONTENT OF SAMPLES EXPRESSED
IN P.P.M. OF DRY PLANT MATERIAL

	<u>COPPER</u>		<u>ZINC</u>	
	POSITIVE	NEGATIVE	POSITIVE	NEGATIVE
Britannia	583	14	33	10
Chapman Camp	7	11	255	37
Texada Island	25	5	6	6

It has been stated before that the mineral content of the various organs of plants vary considerably. The following table shows the percentage of ash in the various parts of plants. The ash is that part of a plant sample remaining after the sample has been heated in a muffle-furnace to about 550° C until all the carbon has been removed. It may be assumed that the ash represents the entire mineral content of the sample, less carbon and a few of more volatile elements such as boron^e selenium and sulphur.

TABLE X

<u>POSITIVE AREA</u>				<u>NEGATIVE AREA</u>	
<u>SPECIE</u>	<u>ORGAN</u>	<u>SAMPLE NO.</u>	<u>% OF ASH</u>	<u>SAMPLE NO.</u>	<u>% OF ASH</u>
Douglas Fir	Cones	2	1.93	18	1.60
	Leaves	1	2.55	17	2.00
	Bark	6	.54	19	.55
	Wood	3	.14	20	.25
Willow	Leaves	112	6.90	118	1.30
	Wood	34	1.80	48	1.25
Lodgepole Pine	Cones	152	.95	175	.40
	Bark	35	1.25	49	1.15
	Leaves	39	1.85	53	1.65
	Wood	29	.25	43	.25

FURTHER WORK IN 1946 - 47

As Dr. H.V. Warren felt that the results of 1945 - 46 investigations warranted further work, the author, aided by E. Jones made a more systematic collection of specimens from the vicinity of the Sullivan mine, Britannia Mine and mineralized areas on Texada Island.

METHOD OF SAMPLING:

Samples were taken from areas adjacent to or directly over the ore bodies, rather than from positive or negative areas to see if the samples adjacent to the ore bodies would show less copper or zinc content than the samples from directly over the ore bodies.

The factors influencing the mineral content of plants apart from the amount of mineral available are:

1. Species of plant.
2. Organ or part of plant.
3. Position of organ on the plant.
4. Age of plant.
5. pH of soil or material surrounding the roots of plant.

To eliminate these variable factors as completely as possible the following method of sampling was adopted.

1. The same species was used throughout in any one group of samples. For example, the samples taken at Barbara Camp Britannia, were all spruce, while those from near the copper plant were nearly all hemlock. The three alder specimens and one douglas fir were taken as control and check samples. The samples taken from near the Little Billy, Cornell, and

Copper Queen Mines on Texada Island were Douglas Fir while those from the Pinto Claim were Hemlock.

At the Sullivan mine Jack pine (*Pinus contorta*) was collected at every sample site, and wherever possible a willow sample was also collected.

2. All the samples from conifers were needles, small twigs and associated cones from the top of the tree. For deciduous samples, leaves were stripped from the whole tree, as the trees were small and all the leaves were needed to get a sufficiently large sample.

3. In all groups only trees of approximately the same age were sampled.

4. All the samples for any one group were taken from a relatively small area, and at the same elevation so that the pH of the soil and drainage conditions should be approximately the same throughout any one group of samples.

About 300 grams of plant material were gathered for each sample, and each sample was packed to camp in a paper bag. At Kimberly and Texada Island, the samples were allowed to dry in air for about one week before being packed in double paper bags and shipped to Vancouver. The samples from Britannia were picked and shipped to Vancouver within a week, and then were allowed to dry for a month with the other samples.

PREPARATION OF SAMPLES FOR ANALYSIS:

The samples, when dry, were ground in a Wiley Mill No. 1

to - 40 mesh. The seive used was brass and will have contaminated the specimens, but all specimens will be contaminated by the same amount and the relative results will not be altered in any way. The mill was cleaned out thoroughly after each sample had been ground. In most cases a stiff brush was all that was needed to clean out the knives and seive. A few of the samples with a high resin content left a very sticky residue around the knives and in the grinding chamber generally. At such times it was necessary to remove the rotary cutter and to scrape away the residue with a knife and then to wash the grinding chamber and rotary cutter with xylene.

METHOD OF ANALYSIS:

The method chosen for the analyses was developed for the detection of small quantities of copper and zinc in soils, and was adapted for the detection of these elements in plant material. Unfortunately the method was too sensitive for the relatively large amounts of these elements present in some of the samples and time did not allow for the further adaptation or decrease in sensitivity. In analyses of this type all apparatus and chemicals must be absolutely free from copper and zinc. Under the existing conditions it was not possible to meet the required standards of purity. Details of the method are reported in Appendix 11 .

The results used in the remainder of this report were obtained by Dr. Delavault whose method is described in Appendix 111. Control analyses were run by Dr. Delavault on material already analysed by Mr. Williams as a check on both

methods of analysis. The control analyses verified the findings of Mr. Williams. In either method the absolute amount of metal reported present may not be correct, but it may be assumed that, relative to one another, the amounts reported are accurate.

RESULTS OF ANALYSES:

At the time of writing only the results for the copper content of the samples from Britannia Camp were available.

The following results are for samples taken from young spruce trees (*Picea sitchensis*) growing near stope 120, at Barbara Camp. For the exact location of samples see Map 1 Page 20.

TABLE XI

<u>Sample No.</u>	<u>Copper expressed as p.p.m. of dry plant material</u>	<u>Copper in % of ash.</u>
B1	18	0.07
B2	21	0.075
B3	9	0.03
B4	5	0.02
B5	9	0.04
B6	12	0.05
B7	12	0.05
B8	6	0.03
B9	16	0.06
B10	25	0.075
B11	15	0.085
B12	10	0.05
B13	16	0.07
B14	8	0.035
B15	17	0.07
B16	12	0.06
B17	5	0.02
B18	11	0.04
B19	10	0.04
B20	12	0.05
B21	6	0.025
B22	8	0.03
B23	22	0.085
B24	7	0.025
B25	7	0.025
B26	12	0.04

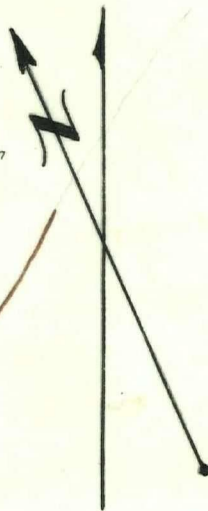
SURFACE MAP
BARBARA

BRITANNIA BEACH BC

Scale 1"=80' Aug. 1946

o Plant Samples

7 Copper in parts per million



120 STOPE

NO. 9 VEIN

3300

4000

4100

4200

NO. 11 VEIN

1-18

02-21

06-12

03-9

07-12

05-9

04-5

08-6

016-12

015-17

09-16

010-25

011-15

012-10

013-16

014-8

019-10

018-11

L.P. 7

17-5

020-12 PP

021-6

022-8

023-22

026-12

025-7

024-7

4000

3900

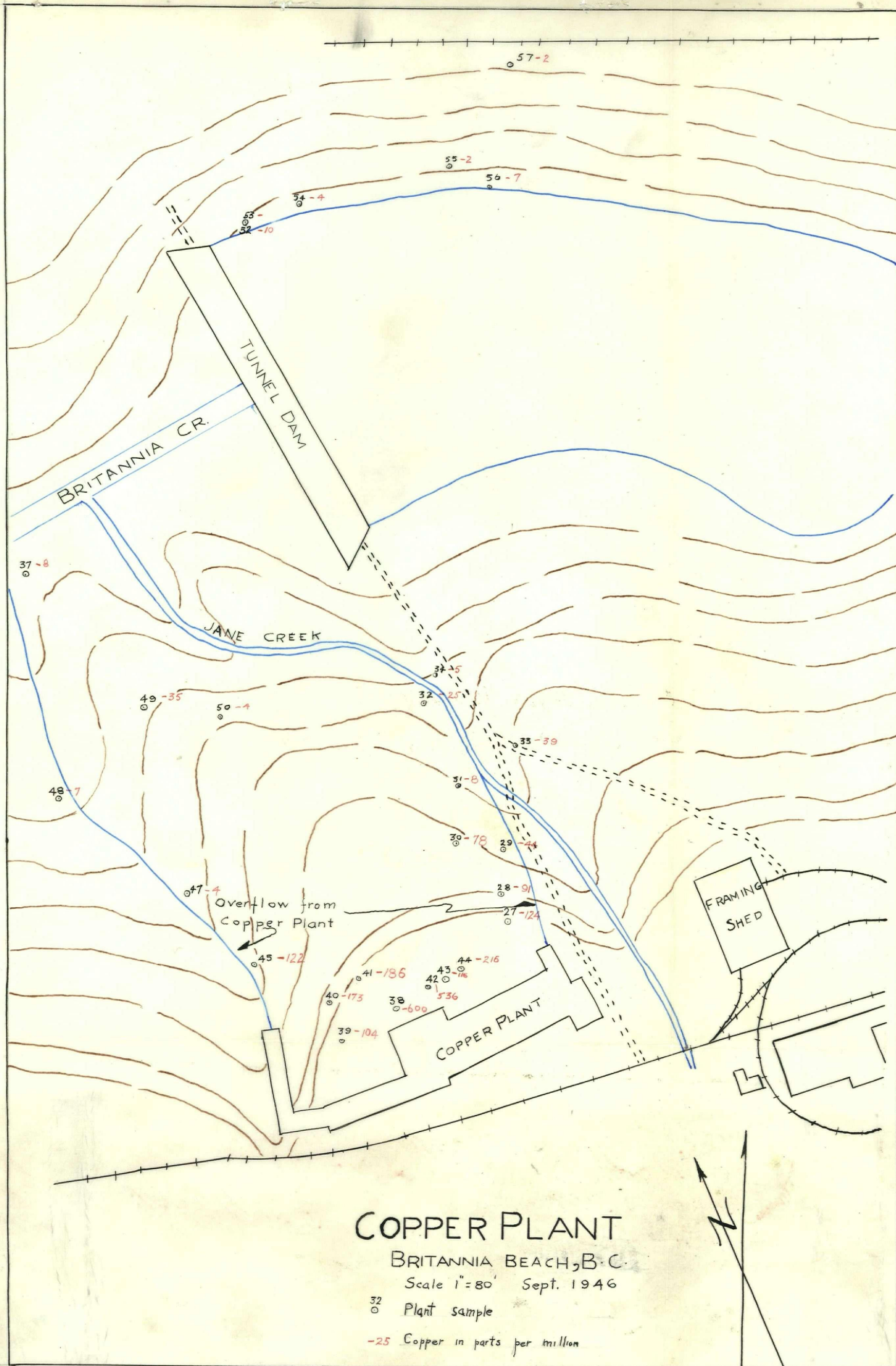
3800

Table XII contains the results from samples collected from the vicinity of the Copper Plant at Britannia. For the exact location of samples see Map 2. Page 22.

TABLE XII

<u>SPECIES</u>				
<u>BOTANICAL NAME</u>	<u>COMMON NAME</u>	<u>SAMPLE NO</u>	<u>COPPER IN PPM OF DRY PLANT MATERIAL</u>	<u>COPPER IN % OF ASH</u>
Tsuga heterophylla	Western Hemlock	B27	124	0.33
		B28	91	0.3
		B29	44	0.14
		B30	78	0.3
		B31	8	0.02
		B32	25	0.07
		B33	39	0.09
		B34	5	0.01
		B37	8	0.02
		B38	600	1.7
Tsuga heterophylla	Western Hemlock	B39	104	0.38
		B40	173	0.55
Alnus rubra	Red Cedar	B41	186	0.53
		B42	536	1.00
Tsuga heterophylla	Western Hemlock	B43	116	0.16
		B44	216	0.53
		B45	122	0.40
		B47	4	0.014
		B48	7	0.02
		B49	35	0.10
		B50	4	0.015
Pseudotsuga taxifolia	Douglas Fir	B52	10	0.025
Alnus rubra	Red Alder	B53	No copper visible	
Tsuga heterophylla	Western Hemlock	B54	4	0.015
		B55	2	0.008
		B56	7	0.02
		B57	2	0.006

The results from samples 1 - 26 would indicate that there is no copper in the vicinity of stope 120. The copper content varies between 5 and 25 parts per million which is in the range of the copper content of plants from negative areas. See Table IX. It was hoped that veins No. 9 and No. 11 would extend laterally beyond the rim of the stope. No evidence of



this lateral continuation was seen at the surface, and from the analyses it would seem that all the copper in the area has been mined. The trees sampled were about ten years old and had probably grown since mining activity in the area had ceased.

On the other hand the samples from near the copper plant, samples 27, 28, 38, 39, 41, 42, 43, 44 and 45, had a very high copper content, from 91 p.p.m. to 600 p.p.m. This concentration is far above the normal found in negative samples. The only explanation for the high copper content in the samples is that there was a relatively high copper concentration in the drainage water from which the trees obtained their moisture. The samples taken north of Britannia Creek, Nos. 52, 53, 54, 55, 56, and 57, although of the same age, of the same species and of similar organs, contained only normal amounts of copper, between 2 and 10 parts per million. The latter samples do not derive their moisture from copper rich ground water, nor is there any indication of mineralization in the rocks below.

The separating tanks within the copper plant may not be absolutely water tight at all times and the seepage from these tanks would enrich the ground in the immediate vicinity of the copper plant. This would explain the very high copper content of samples 38, 39, 40, 41, 42, 43 and 44. Sample 50 containing only 4 p.p.m. was taken from a ridge between the two overflow streams. The low copper concentration would indicate that this sample was too far away from the copper plant to pick up

seepage waters, and far enough away and at a sufficiently high elevation to escape contamination from the overflow creeks.

The other samples are situated intermediately with respect to drainage and seepage, between sample 50 (4 p.p.m.) and sample 38 (600 p.p.m.) This intermediate position is reflected in their copper content which varies, with proximity to copper rich water, from 7 p.p.m. to 91 p.p.m.

CONCLUSIONS

From all the evidence on hand it would appear that vegetation will act as an indicator of the amount of copper present in the rock or soil on which it is growing. The limited results of this report show that vegetation growing near an ore body is not as reliable as an indicator as is vegetation which derives its moisture from copper rich ground water. It is hoped that the samples from the Pinto claim (Texada Island) will prove more satisfactory than those from Barbara Camp. Some of the samples from the Pinto claim were taken from trees growing on rocks in which copper mineralization could be seen.

The writer feels that when satisfactory sampling and analytical methods have been developed, vegetation will be used as a guide to the detection of ore bodies.

APPENDIX IMETHOD OF ANALYSIS OF MR. R.N. WILLIAMS.

The analytical methods employed were essentially those used in normal assaying. Stock reagents and distilled water were employed and blanks were run with every ten samples. However, extra precautions were taken to prevent contamination. The following procedure was carried out.

100 grams of air-dried plant material were ashed in clay crucibles at 600° C. No precautions were taken to prevent loss of volatiles. The resulting ash was weighed and then treated with aqua regia. Concentrated sulphuric acid was then added and the solution evaporated to fumes. The residue was dissolved in water and the solution boiled.

This solution was neutralized with ammonium hydroxide. The iron, aluminium, and occluded salts were filtered out. This precipitate was dissolved in sulphuric acid and reprecipitated with ammonium hydroxide and again filtered out. An excess of ammonium persulphate was added to both filtrates to complete the precipitation of manganese as manganese dioxide. The precipitate was allowed to settle over night, then filtered and washed thoroughly with water. The filtrate was acidified with sulphuric acid and boiled for ten minutes. Then an excess of sodium thiosulphate solution was added until all the copper was precipitated. The precipitate was filtered and washed with hot water. The paper containing the copper subsulphide was then dried and ignited at low temperature. The resulting residue was taken up in concentrated nitric acid

and evaporated to a volume of one c.c. Ten c.c. of water were added. The excess acid was neutralized with sodium acetate and a small amount of sodium fluoride added. The solution was cooled to room temperature and an excess of potassium iodide added. Titration was then carried out with sodium thiosulphate solution equalling one mg. of copper per c.c. of solution.

The filtrate from the copper precipitation was neutralized with ammonium hydroxide, then acidified with hydrochloric acid, and a slight excess added. This solution was brought to boiling and titrated with potassium ferrocyanide solution of a strength equal to approximately one milligram of zinc per c.c. of solution. Uranium acetate was used as an outside indicator. The blanks were made up by using the same amount of reagents as in the normal determinations, and appropriate deductions were then made from the amount found in the unknowns.

The results seemed to be sensitive to within about one part in one million of ash. Analyses reported - do not indicate that the sample contained no copper or zinc, but rather that no satisfactory determination could be made on the amount of sample analyzed.

APPENDIX 11

METHOD OF ANALYSIS ADAPTED FROM PROCEDURE OF R.S.HOLMES

Reagents:

HCl - by constant boiling point method.

NH₄OH - distil concentrated NH₄OH into water in Pyrex container immersed in an ice-bath.

Ammonium citrate buffer - 25% sol. Dissolve 225g of ammonium citrate in 1 litre of H₂O using a large separatory funnel as container. Add conc. NH₄OH, 40 - 45 sol. until solution has a pH of 8.5. Purify by repeated extractions with dithizone reagent and remove excess dithizone by repeated extractions with pure CCl₄

Potassium Iodide solution - 2%. Dissolve 10g c.p KI in 490 ml H₂O. Acidify by adding 5 ml. normal HCl. Add 5 ml. 0.12 sodium sulphite to reduce the free iodine. Shake in a separatory funnel with successive 10 ml. portions of dithizone until no discoloration of dithizone occurs. Discard dithizone extract and remove excess by repeated extractions with pure CCl₄. On standing free iodine may form, which is reduced with Na₂ SO₃ or removed with CCl₄.

CCl₄ - may be used without distillation if pure. Used CCl₄ - first wash with dilute HCl then .02N NH₄OH, drying with anhydrous CaCl₂ and distill.

Dithizone Reagent - dissolve 0.25 g diphenyl thio carbazone in 1 - L. CCl₄ - in a 4L separatory funnel. Let stand at least 15 minutes with frequent agitation. Add 2 L. of 0.02N NH₄OH (40 ml of N. NH₃ to 2 litres). Extract the dithizone into the aqueous layer by vigorous shaking. Discard CCl₄ phase and extract ammoniacal solution of dithizone with 50 ml. portions of CCl₄ until CCl₄ is pure green. Discard CCl₄ phase after each extraction. Add 500 ml. CCl₄ and 50 ml. N. HCl and shake to transfer dithizone to CCl₄. Dilute CCl₄ - dithizone solution

to 2 L with CCl_4 and store in pyrex bottle, painted black, 25 ml of water partly saturated with SO_2 may be added.

Carbamate reagent. - Dissolve 0.2g sodium dithyl dithiocarbamate in 100 ml. H_2O . Filter into a separatory funnel and shake with 5 ml. portions of pure CCl_4 to remove Cu. Prepare a fresh solution for each use.

STANDARD SOLUTIONS OF COPPER AND ZINC

Copper: Accurately weigh 0.1 gm electrolytic sheet copper or any pure metallic copper and dissolve it in 10 ml. dilute HNO_3 . Evaporate solution almost to dryness and add 2 - 3 drops of glacial acetic acid. Transfer the solution quantitatively to a 1 L volumetric flask. Fill flask to mark with H_2O and thoroughly mix.

Zinc: Place exactly 0.1 gm of pure zinc in a 1 litre volumetric flask and dissolve in a mixture of 50 ml. H_2O and 1 ml. concentrated H_2SO_4 . Dilute to mark and mix.

These solutions contain 100Y per ml. Concentration usually used is 1Y metal per 1 ml. To make this concentration pipette out 10 ml. of stock solution into 1 litre volumetric flask and make up to the mark. Such very dilute solutions lose metal ions to the flask wall and must be renewed every day.

Ashing of plant material:

After the samples had been ground to minus 40 mesh in a Wiley Mill, 5 grams of the sample were placed in a clean 50 ml evaporating dish. The samples were ashed in an electric oven at a temperature of 550°C for four hours. Allowed dishes to cool and added 5 drops of redistilled water and then gradually

added to 10 ml. normal HCl. Boiled solution gently for 5 minutes or until all effervescing had ceased. Filtered the solution and adjusted volume of filtrate to 50 ml with N. HCl.

Separation of Copper and Zinc:

Pipette an aliquot, in this case 25 ml. into a 125 ml separatory funnel. Add 5 ml of the 25% ammonium citrate buffer solution. Titrate acidity of solution with NH_4OH to pH 2.5. using thymol blue acid range as an indicator. Immediately after adding the indicator add NH_4OH until red color of indicator begins to turn yellow. Add exactly 5 ml of dithizone solution and shake 5 minutes. Transfer CCl_4 phase to a clean separatory funnel and if first extraction shows considerable excess dithizone, repeat extractions with less concentrated dithizone solution. Combine two dithizone extractions for copper determination and retain aqueous phase for zinc determination.

Determination of Copper:

Add to copper-dithizone solution 10 ml of KI solution and shake for two minutes. Transfer copper dithizone to a clean separatory funnel and free copper dithizone from excess dithizone by shaking for one minute with 50 ml. 6.01 N NH_4OH . The copper may be determined at this point as a dithizonate using a spectrophotometer with light filter 5200A.

Determination of Zinc:

To the aqueous phase from copper-determination add 5 ml more of citrate buffer solution and raise pH to 8.5 by titrating with pure N. NH_4OH , using phenolphthalein as an indicator.

Extract zinc with two or more 10 ml. portions of dithizone. When zinc completely gone the aqueous phase will be orange and the last dithizone extraction should show no color characteristic of zinc dithizonate. Remove the last floating drops and adhering droplets of dithizone by shaking with pure CCl_4 . Combine all zinc dithizone extracts in a clean separatory funnel.

Add to the combined zinc dithizone extracts 50 ml. 0.02 N HCl and shake for two minutes. Allow the phases to separate. Draw off the CCl_4 as completely as possible without letting any of the water enter the stopcock bore, as the zinc has been transferred to the aqueous layer. Rinse out all adhering dithizone droplets with pure CCl_4 and discard the CCl_4 phase.

Add 5 ml. ammonium citrate buffer solution to the 50 ml. 0.02 N HCl and titrate to pH of 8.3 using phenolphthalein as an indicator. Add exactly 10 ml. of dithizone and 10 ml. of carbamate solution and allow phases to separate. At pH 8.3 the diethyl-dithiocarbamate solution inhibits the extraction of iron, aluminum, cobalt and lead by the dithizone solution.

Transfer the dithizone phase to a clean separatory funnel. Remove the excess of dithizone by shaking with 25 ml. .0N NH_4OH and allow phases to separate.

Pipette exactly 5 ml. of dithizone from near the bottom of the dithizone phase to a colorimeter cell and dilute with CCl_4 to 25 ml.

Use light filter 5400A, setting 100% transmission for pure CCl_4 .

APPENDIX IIIMETHOD OF ANALYSIS OF DR. DELAVAUTEstimation of Copper Content of Vegetal Ashes:

5 grs. of dried and milled material are ashed at 650°C (1100°F) in the oven, for 4 - 5 hrs. in an evaporating dish accurately weighed (to $1/2$ mgr.). The ashes are often coloured brown or grey by metal oxides. Weigh accurately the dish with the ashes, to get their weight.

Add 2 ml. of 5 N sulphuric acid into the dish, and evaporate until no more white fumes of Sulphuric develop, in order to expel hydrochloric and excess of sulphuric. Do not overheat. This would decompose sulphates. To reduce Mn_2O_3 , a few drops of concentrated SO_2 solution may be added before heating.

Then add 5 ml. of N/2 sulphuric and mix the solid crust with the liquid, crushing it with a stirring rod. Heat gently without evaporating much, and filter into the electrolytic filtering beaker. The solution must be luke warm; if too hot ($50 - 60^{\circ}\text{C}$) it would boil, splash on the lower part of the tube connecting to the vacuum, and losses would result. Wash twice with about $1\frac{1}{2}$ ml. of water each time, and add 4 drops of concentrated nitric acid. Electrolyze near boiling point, using 0.025 to 0.03 ampere. If the circuit is normal, 0.1 A must pass on short-circuiting the electrodes. Electrolyze 45 min, wash with a beaker of distilled water, remove the cathode from the glass anode holder, and dissolve

the deposit in a few drops of sulphonitric solution: 1 vol. H_2SO_4 , 1 vol. HNO_3 , 2 vols. water. Boil off nitrous oxides, water, nitric acid from the small flask, rinse the cathode and neck with distilled water, add 0.2 gr. sodium acetate, a few drops concentrated potassium iodide, and titrate with N/5 thiosulfate.

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