

## WATER ANALYSES AS AN AID TO GEOCHEMICAL PROSPECTING FOR ZINC IN EAST TENNESSEE

F. DONALD BLOSS

*Department of Geology and Geography  
University of Tennessee*

### INTRODUCTION

Chemical analysis of residual soils is the chief method of geochemical prospecting for zinc in East Tennessee. The method, introduced to the area by Hawkes and Lakin (1949), often permits one to discriminate between soils derived from mineralized rock and those soils derived from rocks lacking mineralization. The possibility exists, however, that some buried ore bodies may escape detection by virtue of the soil cover being derived from the overlying barren rock.

Vogt and Rosenqvist (1942) published determinations of copper in stream water which indicated that water in contact with the weathering products of metallic ore deposits may pick up greater-than-normal trace amounts of the metals involved. The duration and intimacy of contact between the ground water and the ore deposit will, of course, govern the amount of metal taken up by the water. Since even buried ore deposits are likely to be in various stages of mechanical disintegration, oxidation, and solution, the ground water from such an area is likely to be relatively high in metal content upon emergence at the surface. Therefore, the interesting possibility arises that water samples collected at the surface may yield information as to mineralization at depth in the general area.

Several investigators, including Vogt and Rosenqvist (1942), Sergeev (1946), and Huff (1948), have already described examples which indicate the value of water analyses as a guide to the location of ore deposits. Sergeev (1946) noted that a dissected topography and a well developed drainage pattern are essential to the success of the method.

A reconnaissance survey was conducted by the writer during the summer of 1954 to determine whether water analysis could be of value as a forerunner to soil analysis in the geochemical method of prospecting for zinc in East Tennessee. Since the results of the work appear favorable, they are briefly described herein.

### METHODS USED

Water samples were analyzed for heavy metal content by means of a carbon tetrachloride solution of dithizone (diphenylthiocarbazone) in the manner described by Huff (1948). A 0.0016 per cent (weight/volume) stock solution of this reagent (i.e., 0.0457 gms dithizone in 1 lb. of reagent grade carbon

tetrachloride) was stored in a light-proof container in a small portable ice box. From this stock solution two dilute solutions, here referred to as *A* and *B*, were prepared each morning for use the same day. Solution *A* contained one part (by volume) stock to 19 parts pure carbon tetrachloride; solution *B*, one part stock to 59 parts carbon tetrachloride. Aluminum foil wrapped about the containers of these dithizone solutions protected them from light and thereby increased their stability.

Except for the very accurate analytical balance used to weigh out the dithizone for the stock solution, the equipment involved was relatively simple and inexpensive (see Fig. 1). In addition,

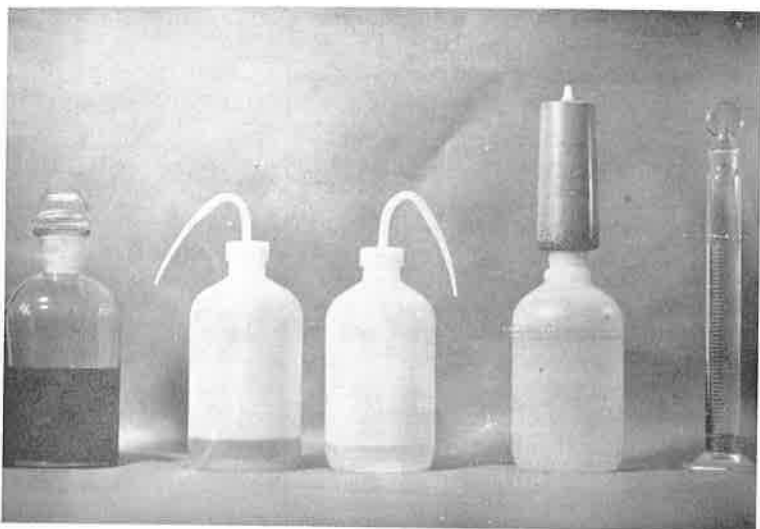


Fig. 1. Equipment used in the field to analyze water samples for heavy metal content. From left to right: (1) One 500 ml. glass-stoppered Pyrex bottle for storing stock solution of dithizone; (2) two 16 oz. squeeze type, polyethylene washing bottles to contain solutions *A* and *B*, respectively; (3) one Deeminac demineralizer 16 oz. bottle with 4 oz. filter for producing metal-free water; (4) one 50 ml. glass-stoppered graduated pyrex cylinder for vigorously shaking 45 ml. of water samples plus 5 ml. of either solution *A* or *B*. As pictured, the pyrex cylinder contains 45 ml. of a water sample plus 5 ml. of solution *B* (settled to the bottom).

a bottle of a standard zinc solution may be useful for periodically checking the strength of *A* and *B* as well as to permit a comparison of a standard water sample of known zinc content with the water samples being tested.

The procedure herein described is rapid and simple. A graduated cylinder is filled with 45 ml. of the water to be tested; 5 ml. of solution *B* is then added and the stoppered cylinder is shaken vigorously for at least 40 seconds. After the droplets of the carbon tetrachloride phase have settled and collected on the

Table 1. The Relationship Between the Zinc Content of a 45 Ml. Sample of Water and the Color Produced in 5 Ml. of Dithizone Solution

Zinc Concentration in Water Sample (p.p.m.)	Colors* Produced in Dithizone Solutions	
	Solution B	Solution A
0.100		49-I-2 } (Reddish)
0.070		49-I-1 } (Reddish)
0.060		49-F-2 } (Reddish)
0.040		49-F-1 } (Reddish)
0.030		51-D-1 (Pinkish)
0.020		52-A-1 (Grayish)
0.010	49-B-1 (Pinkish)	26-G-3 } (Shades of Green)
0.009	50-A-1 } (Almost colorless)	
0.008	50-A-1 } (Almost colorless)	
0.007	25-A-2 } (Shades of Green)	
0.006	25-A-2 } (Shades of Green)	
0.005	25-A-2 } (Shades of Green)	
Color prior to shaking	25-B-4 } (Shades of Green)	25-C-7 }

\*The number-letter combinations presented in this table refer to the plate, column, and row in Macz and Paul's *A Dictionary of Color*, 1st Edition, 1930. For example 49-I-2 refers to the color at plate 49, column I, row 2, which in the writer's judgment closely matched that observed in the 5 ml. of dithizone solution (as viewed with a white background in strong daylight). The graduated mixing cylinder which contained the dithizone was one inch in diameter.

bottom, their color is noted. Comparison of the color with Table 1 permits a semi-quantitative determination of the total metal content of the sample (expressed as zinc). Use of aliquots permits determination of concentrations above 0.010 p.p.m. to within 0.01 p.p.m.; below 0.010 p.p.m. solution B permits discrimination between concentrations less than 0.008 p.p.m. and those of 0.008 or 0.009 p.p.m. Using less than 5 ml. of solution B permits one to discriminate between even lower concentrations of zinc.

For water samples which are very high in zinc or total metal content, it may be necessary to fill the graduated cylinder with less than the 45 ml. ordinarily used, then dilute to the 45 ml. volume by addition of demineralized water. The color obtained by using such a diluted sample containing for example, only 22½ ml. of the unknown water would indicate on Table I a zinc content equal to only one half that of the undiluted unknown. For samples extremely rich in zinc the dilution with demineralized water could be even greater; however, the colorimetrically determined (from Table I) zinc content of the diluted sample would have to be multiplied by an increasingly large factor. Thus determinative errors may be magnified for samples of very high zinc content. In geochemical prospecting, however, only the general magnitude of these high values is important, not the precise value. It is really only necessary to know whether the zinc content of a sample is appreciably more than the background content for the area.

#### SAMPLE SITES

Springs and streams of small volumes and rates of flow were judged to be the most satisfactory sample sites. The main streams of the region were considered unsatisfactory because: (1) there was greater danger of contamination by the cities and towns along the banks; (2) the larger volume would probably dilute beyond detection any relatively high metallic contribution from a mineralized area. Well water was not sampled because of the likelihood of contamination by galvanized plumbing.

#### PRECAUTIONS TO BE OBSERVED

The water sample volume, 45 ml., was maintained for every test, even though for samples of very high zinc content it necessitated dilution of an aliquot with demineralized water. Through this constancy of sample volume the amount of oxygen stopped up and shaken in the cylinder was also maintained constant from one determination to the other. Since dithizone is readily destroyed by oxidation and since solution B, particularly, is very dilute with respect to dithizone content, it is preferable to observe this precaution. In addition, the partition of zinc ions between the aqueous phase and the dithizone phase is no doubt a function of concentration as well as the total zinc present.

Warren and Delavault (1954) noted that large amounts of ferric ion may also oxidize dithizone and thereby prevent the other metals from reacting with dithizone to produce the characteristically colored dithizonates. In this event a yellowish color may be produced.<sup>1</sup> Abundant clay in suspension may also

<sup>1</sup>Hydroxylamine hydrochloride may be used to complex out the ferric ion prior to the sample's addition to solution A or B.

seriously hinder determinations, particularly when the zinc content is low. Since zinc is apparently adsorbed by the clay particles, the determined zinc content will, as a result, be lower than the actual amount.

Contamination of the sample presents the greatest problem in determination of such minute amounts of zinc. All samples with zinc contents higher than the normal background should be run in duplicate. A blank test using 45 ml. of demineralized water should be run periodically to insure that the reagents are free of contamination. Soft glass should not be used; the substitution of a soft glass stopper for the pyrex stopper of the graduated cylinder produced strong positive reactions for heavy metals with solution *B*. Standard zinc solutions when stored in pyrex tend to weaken with age, possibly through transfer of zinc to the container's walls.

#### OBSERVED RESULTS

*Analyses from the Mascot Area.* Analyses were made of both mine and surface waters in the general Mascot area. Several localities within the No. 2 mine of the American Zinc Company were sampled. Results ranged from 0.04 to approximately 0.45 p.p.m. of zinc. Analysis of water dripping down from a diamond drill hole in the ceiling of the 12-level drift revealed a content of more than 0.22 p.p.m. zinc. Water from a crevice in the wall of the main level of the mine contained 0.450 p.p.m., the highest value found. Water from a drainage ditch at this same level contained only 0.06 p.p.m. Mine drainage water at Friends Station contained about 0.09 p.p.m.

Flat Creek was sampled at the surface both upstream and downstream from a mineralized outcrop. The results were 0.005 and 0.007 p.p.m. of zinc, respectively. Streams in the general area usually contained less than 0.005 p.p.m. A few which received mine drainage contained between 0.005 and 0.01 p.p.m. Springs in the area, with one exception, contained less than 0.005 p.p.m.

*Analyses along the Eastern Cumberland Plateau.* Water samples were analyzed from 163 spring or stream sites along the eastern edge of the Cumberland Plateau from the southern to northern boundaries of Tennessee. With a few exceptions the prospects for zinc or lead mineralization appear dim. Of the 163 samples, 146 contained less than 0.003 p.p.m. total heavy metals; 14 contained either 0.003 or 0.004; three contained 0.005 or more p.p.m. total metal. Of the three "highs" one was taken from a stream which proved to have an old automobile carburetor plus additional scrap metal upstream from the sampling site. The other two localities may bear future investigation.

## CONCLUSIONS

Although the work was principally reconnaissance in character, several pertinent conclusions may be drawn:

(1) Ground waters in contact with the zinc deposits of East Tennessee may contain as much as 0.45 p.p.m. zinc.

(2) Surface streams and springs in the Mascot general area usually contained less than 0.005 p.p.m. zinc.

(3) Flat Creek after crossing a mineralized outcrop increased from 0.005 to 0.007 p.p.m. zinc (when sampled during a dry summer).

It thus appears likely that a systematic study of the zinc content of springs and streams in East Tennessee could be of assistance in localizing areas deserving intensive study by more detailed methods. Presumably, the discovery of a zinc-rich stream could be followed by analyses at successively upstream sites, to locate a point where the stream is no longer high in zinc. The area slightly downstream from this point would then be a most promising prospect area for zinc.<sup>2</sup>

With one or two exceptions, the Cumberland Plateau analyses indicate little likelihood that the waters sampled were derived from areas of significant zinc mineralization.

## ACKNOWLEDGMENTS

Grateful thanks are due to the writer's colleague, Dr. Paris B. Stockdale, for his critical reading of the manuscript and to Dr. Charles Oder and Mr. H. A. Coy for their permission to visit the mines and analyze the waters. Mr. Jack Steuerwald guided and assisted the writer in the mines. Portions of this work were done under the auspices of the Division of Geology of the Tennessee Department of Conservation. The writer is further grateful to Mr. William Hardeman, the State Geologist, and to Mr. George Swingle for making the necessary equipment available as well as giving several helpful suggestions. Mr. John Jewell, also of the Tennessee Division of Geology, efficiently guided and aided the writer in securing many of the samples from the Cumberland Plateau.

All views expressed, however, are the responsibility of the writer.

## REFERENCES CITED

- Hawkes, H. E. and H. W. Lakin. 1949. Vestigial zinc in surface residuum associated with primary zinc ore in East Tennessee. *Economic Geology*, vol. 44, no. 4, pp. 286-295.
- Huff, Lyman C. 1948. A sensitive field test for heavy metals in water. *Economic Geology*, vol. 43, no. 8, pp. 675-684.

<sup>2</sup>Copper mineralization might also be a possibility. Warren and Delavault (1954) cite the discovery of an economically important copper deposit by detection of the more mobile zinc at distances from the source where copper was not detectable.

- Maerz, A. and M. Rea Paul. 1930. *A dictionary of color*, McGraw-Hill Book Co., 207 pp.
- Sergeev, E. A. 1946. Issledovanie vod kak sredstvo poiskov polimetallicheskih mestorozhdeni (water analysis as a means of prospecting for polymetallic ore deposits). *Razvedka Nedr*, vyp. 12, no. 2, pp. 51-55. (As translated from the Russian by H. E. Hawkes. *Selected Russian Papers on Geochemical Prospecting for Ores*, by Sokoloff, V. P. and H. E. Hawkes, U. S. Geological Survey Publication, February 1950).
- Vogt, Thorolf and Anna M. Rosenqvist. 1942. Determination of copper in natural waters from the Roras district. (English summary). *Kongelige Norske Videnskabers Selskab*, Forhandling Band 15, pp. 87-90.
- Warren, H. V. and R. E. Delavault. 1954. Water testing in geochemical prospecting. *Mining Congress Journal*, vol. 40, no. 4, pp. 82-85, 99.

## NEWS OF TENNESSEE SCIENCE

*(Continued from Page 262)*

Dr. Alexander Hollaender attended the first International Congress of Human Genetics in Copenhagen in August. Following the Genetics Congress, which ended August 6, Dr. Hollaender participated as special adviser to a study group being convened by the World Health Organization in Copenhagen to discuss the effect of radiation on human genetics. Dr. Hollaender then went to Stockholm for the Fifth International Radiobiology Congress. He served as chairman of the session on "Irradiation Effects on the haematopoietic system" and presented a major paper before the Congress entitled "The effects of pre- and post treatment on the radiation sensitivity of microorganisms."

Dr. Sheldon Wolff presented a paper entitled "Recent Studies on chromosomes breakage and reunion" at the Fifth International Congress on Radiobiology in Stockholm in August. Following the Radiobiology Congress, Dr. Wolff remained in Stockholm to attend a symposium on Induced Mutation held at the Statens Skogsforskningsinstitut. Dr. Wolff visited several other scientific laboratories while in Europe.

The following personnel additions have recently been made in the Biology Division: Dr. Edward Novitski will head the *Drosophila* group of the Cytology and Genetics section; he was formerly in the Department of Zoology, University of Missouri. Dr. George S. Brosseau, Jr., formerly with the Department of Genetics, University of California, has also joined the Cytology and Genetics section. Dr. Laurence M. Sandler, formerly with the Department of Zoology, University of Missouri, will be Research Associate for 1956-57 with the *Drosophila* group. Mrs. Iris L. Sandler will be with the *Neurospora* group. Dr. Robert Rabson has joined the Biology Division and is associated with the Plant Biochemistry group; Dr. Rabson was formerly a student in the Department of Botany, New York State College of Agriculture, Cornell University.

The University of Tennessee has been awarded a \$10,000 contract by the Atomic Energy Commission to study vegetation grown in soil contaminated by radioactive wastes. The study will be directed by Dr. Royal E. Shanks of the Department of Botany. He will be assisted by Dr. L. F. Seatz, agronomist with the Agricultural Experiment Station, and John T. McGinnis, graduate assistant in Botany. The work will be done in cooperation with the Oak Ridge National Laboratory.

*(Continued on Page 324)*