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Dithizone Field Test
Some Suggestions

By

Paul L. Anderson

and

Robert Pelz

College, Alaska

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D I T H I Z O N E F I E L D T E S T
S O M E S U G G E S T I O N S

During the course of the Laboratory's work on our various geochemical procedures some pertinent factors about the dithizone field test resulted. The following are comments on the variations obtained and some suggestions as to how to reduce the variation and obtain greater confidence in the method.

Each geochem kit should contain either a solution with known zinc, or a standard sediment sample that contains extractable zinc, that can be used to test the dye solution. We have prepared such materials for your use.

Under the best of conditions the field test is not highly reproducible. On a number of samples with up to ten titrations each, the standard deviations averaged about 2 ml with range of about 50% of the value. These values were obtained in the laboratory under nearly ideal conditions. We have found that:

- 1) The number of strokes, speed, rhythm, and vigor of shaking constitute major variables. These factors must be rigidly standardized for best reproducibility. Shake slowly, for 50 strokes, counting each down-stroke.
- 2) The end-point should be observed in bright light away from colored objects. Observing the end-point against a white paper is probably best.
- 3) Evidently some organic matter can completely bleach the dye to colorless. In those cases the sample is just not amenable to this test.
- 4) In some cases the dye does not separate from the mud-water mixture and the dye color cannot be seen. In such instances the sample can be hand centrifuged by swinging the cylinder on the end of a stout fishing line (with a swivel). This is, of course, cumbersome but it does facilitate handling certain difficult samples.
- 5) Contamination from the sample-spoon, dirty cylinder, and fingers is a serious problem. Wash the cylinder, stopper, and spoon thoroughly. Never touch any item with your fingers that is to come in contact with the solutions. After washing the spoon and stopper do not wipe because of the likelihood of contaminating the solutions - just wash thoroughly.
- 6) Because of the variation in the test, whenever color from a sample is found it may have geochemical significance. You should probably be willing to run those samples three or four times to establish the degree of significance, i.e., the spread and average value.
- 7) Make an effort to use fine sediment only with a minimum of organic matter.
- 8) We have found it useful during the analysis to have a cylinder of fully titrated dye for direct end-point comparisons.

DITHIZONE FIELD TESTS

FIELD PROCEDURE

1. Measure one level scoopful (0.1 to 0.2 cc) of sample, and tap into graduated cylinder.
2. Add 5 ml of extractant (see Extr-HM below) to 5 ml mark.
3. Add 1 ml of dithizone solution (see Dz-HM below).
4. Insert stopper and shake briskly 50 times or until the dithizone solution is red, whichever occurs first.
5. Allow dithizone solution to collect at surface of liquid and observe color. If green, record 0; if blue, or blue-gray, record 1; and if purple or red, proceed with step 6.
6. Add 1 ml more of dithizone solution and shake briskly 50 times or until solution is red, whichever occurs first. If color is blue, record 2, if purple or red, repeat the shakeout adding dithizone solution in increments of 2, 4, 4, and 4, until blue or blue-gray endpoint is reached. Record total volume of dithizone solution needed. If the endpoint is overshot, the recorded value may be interpolated.
7. In the field procedure, the time and vigor of the shakeout should be the same for all determinations.

HEAVY-METAL EXTRACTANT (Extr-HM)

A five times strength ammonium citrate solution to be diluted 4:1 with metal-free water for field use.

DITHIZONE SOLUTIONS

1. Carefully weigh out 0.01 g of dry dithizone crystals.
2. Add to 100 ml of toluene (benzene, xylene, chloroform, or carbon tetrachloride may be substituted), and allow about an hour to dissolve. This is the stock solution from which the field dithizone solutions for both the heavy-metal and copper tests are prepared.
3. Add stock solution to toluene xylene or benzene in a proportion of 1:9. This is the field dithizone solution for the heavy-metal test (Dz-HM). It should be protected from heat and light.

GENERAL NOTES

Zinc, copper, and lead are the principal heavy metals, measured (as a group), in this test. The sensitivity of the determination of zinc is considerably higher than that of either copper or lead.

POOR REPRODUCIBILITY OF DATA

Failure to reproduce results may be due either to variability in the samples or to lack of standardization of the analytical technique. Non-reproducibly analytical data in presumably identical samples may appear as a result of a variety of factors. A sample high in organic matter not uncommonly contains a much higher concentration of metal than a non-organic sample from the same locality. Another effect is that the organic matter in the sample may cause a spuriously high reading due to partial fading of the dithizone. Clay-sized material normally contains a higher concentration of metal than coarser material;

thus variability in grain size of a sample can lead to poor reproducibility. These effects can be reduced by restricting samples so far as possible to material with the same grain size and the same content of organic matter. If particles of minerals like malachite that contain the metal as a dominant constituent occur in the sample, a random variation in the number of such particles will cause wide variations in reported values of contained metal. This effect can be reduced by fine sieving.

The principal analytical source of error in the dithizone field tests is in standardizing the time of shaking. The so-called "extractable" metal content of a sample is not an absolute quantity. It is normally greater the longer the extractions stay in contact with the sample. Thus the time between the beginning of the extraction and the time the colors are estimated is very critical and should be carefully standardized. Another source of analytical error comes from the yellowing and fading of the dithizone solution. As the solution deteriorates, the values as read tend to become progressively greater. Stock solution is considerably more stable than the more dilute field solution.

EXTRACTION OF METAL FROM SAMPLE

The first reaction in both the heavy-metal and the copper test is the extraction of the metal out of the solid sample and into the aqueous solution. This reaction starts as soon as the extractant first comes in contact with the sample. In the heavy-metal test, the extractant is a slightly alkaline solution of ammonium citrate. This reagent will solubilize a large fraction of the metal held by ion-exchange forces on the surface of particles of organic matter and clay minerals, and a lesser fraction of the metal contained in freshly precipitated limonite. Metal held in residual and detrital minerals is removed very slowly and incompletely.