

A NEW MICROCHEMICAL TEST FOR SELENIUM

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In the course of an investigation of microchemical methods as applied to the identification of minerals, the writer has found a test for selenium that does not seem to have been described heretofore. The test appeared to be so highly satisfactory that it was worked out in detail to find the conditions under which the reaction took place and the possible interference that might be caused by the presence of other elements in the test solution.

A number of tests for selenium have been described and are in general use. The most widely used test depends on the precipitation of the element from a hydrochloric acid solution by addition of stannous chloride solution.¹ The product is a brick-red, amorphous precipitate of selenium. This test is sensitive and characteristic but unfortunately the reagent will also precipitate tellurium, gold and mercury, and these may obscure the selenium. Another test for selenium uses potassium iodide to precipitate a reddish-brown powder of selenium iodide.² It has been found, however, that a number of elements, notably tellurium, copper and gold, also give precipitates with potassium iodide and that the products are sometimes indistinguishable from the selenium reaction.

The new test, using the organic compound, thiourea ($\text{SC}(\text{NH}_2)_2$), has the advantage that the very highly colored product is distinctive and by observing certain precautions hereafter described, it is specific and not interfered with by other elements in the test solution. The test is made in cold, dilute hydrochloric acid solution by adding a drop of 10 per cent thiourea solution in water to a drop of the test solution on a glass slide. On adding the reagent, long streamers of a fine, amorphous, brilliantly red precipitate slowly spread across the drop. By transmitted light the precipitate ranges in color from very dark blue to purplish red, but by directing the light source onto the top of the slide the characteristic brilliant red color can be seen. The appearance of this precipitate is very characteristic under the microscope and can be recognized in concentrations down to less than 0.01% Se, but it is so highly colored that in most cases it will be plainly visible to the unaided eye.

Of all the common elements tested, only copper, gold, mercury and bismuth react with the reagent or interfere with the selenium test. Copper produces a precipitate with thiourea which is white by reflected light

¹ Short, M. N., *Microscopic Determination of the Ore Minerals*, U. S. Geol. Survey, Bull. 825, 1931.

² Short, M. N., *idem*.

and dark brownish by transmitted light. Mercury produces a colorless, crystalline precipitate. Bismuth forms a clear, yellow solution with thiourea. Gold forms an immediate blue-black precipitate which redissolves and does not interfere further. These reactions are seldom strong enough to mask the brightly colored selenium precipitate, but interference by these elements can be largely obviated by the following procedure.

A minute fragment of the mineral to be tested is broken down on a glass slide with a drop of 1:1 HNO_3 . Part of the selenium in the mineral is precipitated as the element in a red, glutinous mass or a red powder which is not attacked by HNO_3 , HCl or aqua regia. The rest of the selenium is deposited as a white residue of H_2SeO_3 . This is sparingly soluble in 1% HNO_3 and H_2O , distinctly more soluble in 1:7 HNO_3 , and readily soluble in 1:5 HCl . Leach the residue from the decomposition with 1% HNO_3 to remove copper and finally with a drop of water, removing both drops. Then leach with a drop of cold 1:5 HCl , transfer the drop and test with thiourea for selenium.

The same procedure will also eliminate mercury from the residue although most mercury compounds must be broken down with aqua regia. If the mineral is not decomposed by 1:1 HNO_3 , aqua regia is used and the residue is leached as above with 1% HNO_3 , thus removing mercury.

Bismuth reacts with thiourea to form a clear, yellow solution. The reaction is sensitive enough that it has been recommended by Watson as a spot test for bismuth.³ The character and color of the product is so different from the selenium reaction that bismuth will not mask even very small amounts of selenium. Selenium will mask bismuth but if the test drop is filtered or allowed to settle, both elements can readily be recognized in the presence of one another.

Gold, as noted above, forms a precipitate with thiourea but this redissolves in excess thiourea and there is no further color reaction and no interference with the selenium reaction. Moreover, gold is also eliminated from the test solution under the procedure given above for preparing the solution.

The following elements were tested in 1% solutions to determine their reactions with thiourea and the effects they might have on the selenium reaction: As, Au, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Sn, Te, Ti, and Zn. Mercurous mercury and silver cannot appear in the hydrochloric acid solution. With the exceptions noted above, none of

³ Watson, J. Adam, Colour reactions in the micro-chemical determination of the elements: *Mineral. Mag.*, vol. 24, pp. 21-34, 1935.

these elements interferes. Moreover, it should be remarked that the selenium precipitate is the only intensely colored reaction given by any of the common elements with thiourea. Thus, selenium can be detected even in the presence of large amounts of copper, mercury or bismuth. The greatest advantage of the test, aside from its extreme sensitivity, is the fact that the product with selenium is wholly dissimilar from that given by any other common element.

This test appears much more satisfactory to the writer than either of the common microchemical tests used in mineralogical identification. Both stannous chloride and potassium iodide precipitate many elements whose products may obscure one another, whereas this reaction is very sensitive, the colored product is unique, and it can be made specific. The nature of the precipitate is not known but it is presumed to be a complex organic compound since it is quite different from the elemental selenium precipitate produced by stannous chloride.

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PROCEEDINGS OF SOCIETIES

PHILADELPHIA MINERALOGICAL SOCIETY

Academy of Natural Sciences of Philadelphia, April 1, 1937

Mr. Arndt presided at a stated meeting, with 39 members and 35 visitors present. Messrs. Richmond E. Myers, John S. Penny, and George R. Cope were elected to membership.

Participation in the Hobby Show at the Commercial Museum, May 10th to 15th, with exhibits of mineral specimens, was approved. Mr. Morrell G. Baldwin spoke on "Ancient and Medieval Gemology."

Albert Jehle reported malachite and quartz crystals from Bridgeport, and Edwin Roedder exhibited thorianite, gummite, and uranophane from Easton, and jeffersonite and calcite from Franklin, New Jersey.

May 6, 1937

A stated meeting was held with Mr. Arndt in the chair, 49 members and 33 visitors were in attendance. The deaths of J. Rady Miller, and Fred Hilbiber were announced.

Dr. J. D. H. Donnay, assisted by Dr. David Harker, of Johns Hopkins University, addressed the society on his new law of crystallography, which is a further development of the Law of Bravais. The use of perforated cards (representing properties of minerals) in the determination of non-opaque minerals was demonstrated.

A number of trips were reported, and many specimens were exhibited: W. H. Flack, collected at Easton, Pa. (aragonite, asbestos, eastonite, gummite, thorianite, uranophane); Leonard Morgan, at Bernardsville, N. J. (natrolite); at Prospect Park, N. J. (amethyst, chabazite); George R. Cope, at Unionville, Pa. (chesterlite, beryl, corundum); Samuel G. Gordon, at Grafton, N. H. (apatite, uraninite, uranophane, autunite); Edwin Roedder, at Unionville, Pa. (beryl); Louis Moyd, at Sparta, N. J. (allanite).