IDENTIFICATION OF THE OPAQUE MINERALS BY ELECTROCHEMICAL METHODS

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Abstract

A relatively large group of species fail to react with the etching reagents which are used in the standard methods of identification of opaque minerals. This group may be subdivided by the electrolyzation of a drop of etch reagent on a polished surface of the mineral. The results obtained with electrolyzation by means of both alternating and direct currents are presented.

Introduction

Opaque minerals in polished section are commonly identified by applying a drop of reagent to the surface of the mineral grain and noting whether or not the grain has been etched or otherwise affected. By application of a standard set of reagents in consecutive order it is thus possible to place any mineral in a particular group. Useful tables for this method of identification have been compiled by numerous authors.*

Each of these tables contains a sizable group of minerals which do not respond to any of the reagents, or if they do respond, their reactions are only faint and indefinite.

The purpose of the work described in this paper was to devise a method of subdividing this group of resistant minerals. This can be done in one, or both, of two ways: (1) By getting the mineral into solution in some manner, so that microchemical tests can be carried out to determine its constituent elements; or (2) by producing distinctive stains or etch patterns on certain minerals, thus distinguishing them from others which refuse to react.

To accomplish these results, an electric current was passed through the drop of reagent on the mineral surface. Some of the minerals tested in this manner went into solution readily, whereas their solubility in the reagent is negligible if no current is applied. Examples of this type are cassiterite, franklinite, sphalerite, and chalcopyrite. Microchemical tests could then be applied to determine the elements present.

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* Murdoch, Joseph, Microscopic Determination of the Opaque Minerals, New York, **1916.**

Davy, Myron W., and Farnham, C. M., Microscopic Examination of the Ore Minerals, New York, **1920.**

Schneiderhöhn, H., Anleitung zur Mikroscopischen Bestimmung und Untersuchung von Erzen und Aufbereitungsprodukten, Berlin, **1922.**

Schneiderhöhn, H., and Ramdohr, P., Erzmikroskopische Bestimmungstafeln, Berlin, **1931.**

Short, M. N., Microscopic Determination of the Ore Minerals, *Bull.* **914,** *U. S. Geol. Survey,* **1940.**

Some minerals stained readily and distinctly. Intergrowths of franklinite and magnetite can be brought out by this staining procedure. Franklinite will stain a brownish-black when an alternating current is passed through either HNO_3 or HCl, while any intergrown magnetite will remain unaffected. Hematite can be distinguished from ilmenite, in that hematite can be stained by passing a direct current through a drop of KCN on the mineral surface, whereas ilmenite is negative to all of the reagents used, both with alternating and direct currents.

PREVIOUS WORK

The first mention of the use of electrolysis in the identification of opaque minerals, so far as the writer can find, was that by Davy and Farnham,[1] who described reactions with some of the copper minerals. Schneiderhöhn[2] employed electrolytic etching, but rather for the purpose of bringing out textures of minerals than for identification. McKinstry[3] described results of electrolytic staining and etching on most of the common and a few of the rare minerals, but did not investigate all of the minerals of the group listed in the standard texts as "negative to all reagents." Of those which he tried, all but sphalerite gave negative results with a direct current of low voltage. In the present work additional minerals have been investigated, and higher voltages were used with both alternating and direct currents.

PROCEDURE

The work carried on consisted of observing the effects of electrolyzing a drop of the standard etch reagents while in contact with a polished surface of the mineral. The method used is essentially the same as devised by McKinstry, except that the present scheme avails itself of the effects produced by both alternating and direct currents, whereas the former was concerned with direct current only. Also a slightly higher voltage (between four and six volts) was used in view of obtaining more determinative results with less time.

The apparatus (Fig. 1) consists of a pair of platinum wires which are sealed into a six-inch section of two-holed, one-quarter inch, porcelain insulating tubing, one wire in each hole. The platinum wires are connected within the tube to a pair of lead-out wires. When used with direct current, these lead-out wires are connected to wires which originate at three dry cells and pass through a reversing switch. This arrangement

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[1] Davy, Myron W., and Farnham, C. M., *op. cit.*, p. 9.

[2] Schneiderhöhn, H., *op. cit.*, p. 120.

[3] McKinstry, H. E., Magnetic, electrochemical, and photochemical tests in the identification of opaque minerals: *Econ. Geol.*, **22**, 830–843 (1927).

allows either of the poles to be made positive or negative. When used with alternating current, the lead-out wires are connected to a six-volt step-down transformer. By connecting light bulbs of various wattage into the primary circuit, the voltage can be decreased to suit the needs. The tube is mounted on a ring stand or other holder in such a manner as to be free to rotate on its longitudinal axis, as well as being free to swing in and out beneath the microscope objective.

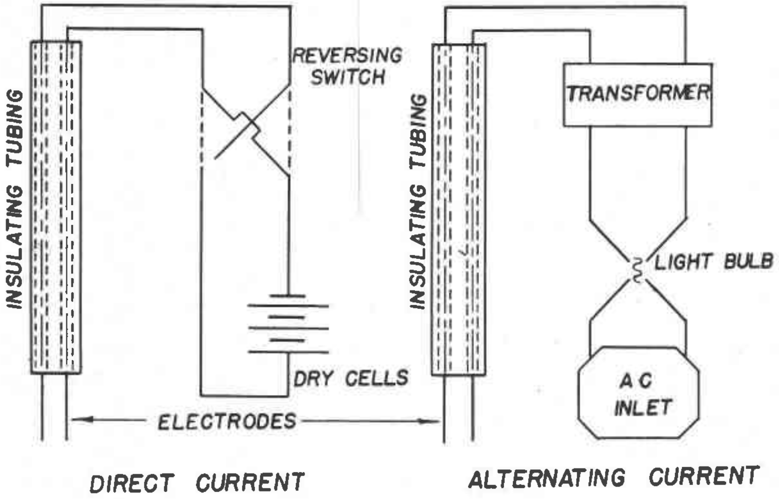

Fig. 1. Diagram of Apparatus.

Unless otherwise indicated, the tests consisted of immersing the electrodes into a drop of the etch reagent until they made a firm contact with the mineral surface. In most instances, the current was passed through this circuit for a period of two minutes. If a time other than that just indicated was used, it will be specifically noted.

In some cases an attempt was made to stimulate the reactions by heating the electrolyte. To accomplish this, the electrodes were "arced." That is, the two platinum wires were bent so as to contact each other. They then became red-hot, and formed a convenient method of heating the reagent. However, though this procedure seems to offer possibilities, it was not thoroughly investigated.

The reagents used throughout the course of this work are the same as those described by Short.[4]

The technique of making the microchemical tests for the elements is as follows: After the current has been passed through the electrolyte for the

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[4] Short, M. N., *op. cit.*, p. 184.

desired time, the electrodes are removed. The reagent which remains on the polished surface (hereafter referred to as the residues of staining) is drawn up with a capillary tube, and transferred to a clean glass slide. The desired tests are conducted on the solution.

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BEHAVIOR OF MINERALS

CASSITERITE

AC—HNO_3—A slight stain, mostly water soluble.
  HCl—Mineral lightened to a cream color in places. Some stains are gray in center and are surrounded by blue and brown zones.
  KCN—Some areas stain light brown. Not dependable.
  $FeCl_3$—Small light brown stain where electrodes made contact.
  KOH—Negative.
  $HgCl_2$—White deposit on specimen.
DC—HNO_3—Negative.
  HCl—A smoky brown stain with a pit where the electrodes made contact. Brings out scratches (polishing?) on mineral surface.
  KCN—Stain is brown on outer edges. Sometimes dark gray, sometimes blue in center.
  $FeCl_3$—A small brown to iridescent stain under the anode.
  KOH—Negative.
  $HgCl_2$—A brown to black stain.

Tests for tin, by means of cesium chloride, with the residues of the HCl stain proved faint.

CHALCOPYRITE

AC—HNO_3—(30 seconds) A zoned, brilliantly iridescent stain surrounding two black pits where the electrodes made contact.
  HCl—(30 seconds) A brilliant, differentially iridescent stain surrounding two black pits where the electrodes made contact.
  KCN—(10 seconds) A brown stain surrounding two black pits where the electrodes made contact.
  $FeCl_3$—(10 seconds) Two stains; black to gray in the center, surrounded by jagged iridescent zones.
  KOH—(10 seconds) Stain is black in center surrounded by zones of blue and gold.
  $HgCl_2$—(10 seconds) Similar to KOH stain, but mainly blue and gold.
DC—HNO_3—(10 seconds) Brilliant iridescent zones under both electrodes.
  HCl—(10 seconds) Black to iridescent stain, zoned under anode.
  KCN—(30 seconds) Red stain under anode, pit under cathode.
  $FeCl_3$—(30 seconds) Brilliant iridescent stain under anode.
  KOH—(30 seconds) A zoned, brilliantly iridescent stain under anode, iridescent to black under cathode.
  $HgCl_2$—(10 seconds) Brilliantly iridescent under both electrodes.

Tests for copper by means of potassium mercuric thiocyanate with the residues of the HNO_3 and HCl stains are very strong. However, faint to fair tests for iron and copper can be obtained without application of an electric current.

CHROMITE

AC—Negative to all reagents.
DC—Negative to all reagents.

When the electrodes are arced and applied to a drop of H_2SO_4 on the specimen, two small pits surrounded by pale chromatic rings result.

FRANKLINITE

AC—HNO_3—Brownish black stain.
  HCl—(1 minute) Brownish black stain with pits where electrodes made contact.
  KCN—Smoky brown stain with black pits where electrodes made contact.
  $FeCl_3$—Same as KCN stain.
  KOH—A zoned, brown to iridescent stain around each electrode.
  $HgCl_2$—Black to iridescent stain.
DC—HNO_3—Negative.
  HCl—Negative.
  KCN—Differentially iridescent to black stain.
  $FeCl_3$—Negative.
  KOH—Negative.
  $HgCl_2$—Stain is differentially buff, brown, and black.

Tests for iron by means of potassium mercuric thiocyanate can be obtained with two minute staining without application of an electric current. However, with the application of current for one-half minute with *AC*—HNO_3 or *AC*—HCl, a good iron test can be obtained.

HEMATITE (Specular)

AC—Negative to all reagents.
DC—HNO_3—Negative.
  HCl—Negative.
  KCN—Brown to iridescent stain.
  $FeCl_3$—Negative.
  KOH—Negative.
  $HgCl_2$—After about one-half minute the mineral becomes coated with a white precipitate which then seems to arc the current across the mineral surface and stain it brown to black. This stain was attempted with the cathode off the mineral, but still in the reagent, and the anode in contact with the mineral within the drop of reagent. This resulted in a slight stain under the anode, while the cathode appeared to pick up metallic mercury. Reversing the position of the electrodes resulted in the usual stain.

HEMATITE (Red)

AC—Negative to all reagents.
DC—Negative to all reagents.

ILMENITE

AC—Negative to all reagents.
DC—Negative to all reagents.

Staining with $HgCl_2$ produces a faint white coating on the mineral surface.

Arcing the electrodes in a drop of H_2SO_4 produces a black stain. If borax is fused on top of this stain by arcing the electrodes while in contact with the borax, the resulting bead is a very pale yellow (hot).

MAGNETITE

This mineral is negative to all reagents unless the electrodes make a firm contact with the specimen. Under these conditions the mineral surface becomes hot, as do the electrodes, and the mineral will stain with any of the reagents, or a heat stain can be produced without any reagent.

AC—HNO_3—Two pits where the electrodes contacted, surrounded by a brownish gray stain.
- HCl—Similar to HNO_3 stain.
- KCN—A black stain.
- $FeCl_3$—A small brown stain.
- KOH—Brownish black stain where electrodes made contact, surrounded by a zoned, brilliantly iridescent stain.
- $HgCl_2$—Immediate precipitation of a white compound which then stains black, brown, and iridescent.

DC—Stains similar to *AC* stains.

Tests for iron by means of potassium mercuric thiocyanate are very strong with the residues of the HNO_3 and HCl stains. However, faint iron tests can be obtained without application of an electric current.

RUTILE

AC—Negative to all reagents.
DC—Negative to all reagents.

SPHALERITE

AC—HNO_3—Circularly zoned, iridescent stain.
- HCl—Dark gray stain, pitted in the center and with iridescent bands near the outer margins.
- KCN—Negative.
- $FeCl_3$—Slight gray stain with pits where the electrodes contacted.
- KOH—Negative.
- $HgCl_2$—Negative.

DC—HNO_3—Slight brown stain.
- HCl—Large brown smoky stain with pits where the electrodes made contact.
- KCN—No stain; brings out mineral cleavage.
- $FeCl_3$—(1 minute) Pit where electrodes made contact, fumes tarnish grayish brown, cathode collects black coating.
- KOH—No stain, but a white precipitate develops when water is added to the reagent remaining on the mineral surface.
- $HgCl_2$—Fumes stain grayish brown, pit where electrodes contacted.

Tests for zinc by means of potassium mercuric thiocyanate are very strong with the residues of the HNO_3 and HCl stains. However, faint to good tests can be obtained from the residues of staining without application of an electric current.

WOLFRAMITE

AC—Negative to all reagents.
DC—Negative to all reagents.

TABLE FOR MINERAL IDENTIFICATION

AC		DC			
HNO_3	HCl	HNO_3	HCl		
+	+	+	+	Isotropic	Anisotropic
				Chalcopyrite Magnetite Sphalerite	Chalcopyrite
		−	+		Cassiterite
		−	−	Franklinite	
−	+	−	+		Cassiterite
−	−	−	−	Chromite Hematite Magnetite	Hematite Ilmenite Rutile Wolframite

CONCLUSIONS

The results presented here indicate that electrochemical methods offer a convenient aid in the identification of minerals of the "insoluble group." These results are based on a relatively small number of specimens, and in order to be thoroughly reliable ought to be checked on material from many localities. However, the results are consistent as far as they go, and as the writer will be unable to continue the work, he is presenting his results in the hope that it will prove useful, and that it will stimulate further investigation by others.