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The Determination of the Points of Zero Charge of Fine Mineral Particles by a Titration Technique

By D. A. Stanley, P. M. Brown, and B. J. Scheiner

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THE DETERMINATION OF THE POINTS OF ZERO CHARGE OF FINE MINERAL PARTICLES BY A TITRATION TECHNIQUE

by

D. A. Stanley,[1] P. M. Brown,[2] and B. J. Scheiner[3]

ABSTRACT

The Bureau of Mines has developed a simple titration technique for determining the points of zero charge (PZC) on minerals. The technique consists of titrating a mineral slurry with the potassium salt of polyvinyl sulfuric acid (PVSK) in the presence of an indicatory dye and a positively charged polymer. Values obtained by this simple method are in good agreement with values found in the literature.

INTRODUCTION

The Bureau of Mines is investigating the fundamentals of fine particle flocculation as part of its mineral science research effort. Ultrafine particles generated during the processing of ores and minerals are often dewatered by flocculation techniques. High-molecular-weight polymers are added to the fine particle slurry, which agglomerates the fine material into larger aggregates that dewater at a rate fast enough to be handled in conventional equipment such as thickeners and filters.

The type of flocculating reagent used will vary depending on the surface properties of the individual particles contained in the slurry. In fact, the performance of flocculating agents often depends on the adsorption of the flocculating agent on the mineral particulate. Adsorption is affected by such properties as the pH of the slurry and the magnitude and sign of the charge on the mineral particle. A method often used to determine the charge on the surface of the mineral is zeta potential measurement. This is accomplished by placing a sample in an electrophoresis cell and observing the effect of an electrical field on the particle. When dc voltage is applied to the cell, the particles that are electrically charged move toward the oppositely charged electrode. The particle velocity, which is measured by timing individual particles on a microscope grid, is porportional to the electrophoretic mobility. The potential gradient and mobility permit calculation of the zeta potential, which is a function of the surface charge.

It has been observed that, for many minerals, flocculation efficiencies increase as the zeta potential approaches zero. The pH at which the zeta potential is zero is defined as the point of zero charge (PZC). To determine the PZC for a mineral, zeta potential measurements are taken at various pH values. This usually requires a large number of measurements, which are often tedious and time consuming.

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This report describes a simple titration method for determining the PZC, as an alternate to zeta potential measurements. Values of the PZC for a variety of minerals were determined and compared with values found in the literature.

MATERIALS, PROCEDURE, AND METHODS

Mineral samples used in the PZC studies were obtained from Wards Natural Science Establishment.[4] The samples were ground and screened at 325 mesh. The minus 325-mesh material was used for the experiments without further treatment. The titration method is based on a colloid titration technique used to control coagulant dosage in water titration (6-7).[5] The PZC is determined by titrating the fine particles with a polymer of known charge. The endpoint is indicated by use of an organic dye, generally toluidine blue, which changes from blue to purple in the presence of a negative colloid. First, an excess of a positive polymer is added to the fine particles for which the PZC is to be determined. The exact amount of excess positive polymer is then determined by titration of the mineral slurry with a standard negative polymer, the potassium salt of polyvinyl sulfuric acid (PVSK). The PVSK solution is added until the indicator dye changes to purple, indicating the endpoint. A second titration is conducted on a blank containing only the positive polymer and the dye. The charge on the mineral is determined by taking the difference between the amount of PVSK solution required to titrate the mineral sample and the amount required to titrate the blank. If the mineral is negatively charged, the difference will be negative. If the mineral is positively charged, the difference will be positive.

To determine the PZC, the titration is conducted at various pH values. The charge on the mineral at each pH is determined as mentioned, by taking the difference between the amount of PVSK needed to titrate the sample and the blank. The pH at which this difference is zero is the PZC of the sample.

The titration tests were conducted on dilute aqueous slurries of the fine particles, ranging from 0.02 to 0.2 wt-pct solids. Titrations were conducted using a 0.010-pct solution of Eastman Kodak PVSK as the negatively charged reagent and a 0.005-pct solution of Cyanamid Superfloc 330 (a highly cationic polyamine) as the positively charged reagent. The indicator solution was prepared by dissolving 175 mg of Eastman Kodak toluidine blue in 100 ml distilled water.

The titration procedure was as follows: 25 ml distilled water, 4 ml mineral slurry, and 1 ml Superfloc 330 solution were blended together, and the sample volume was brought up to 50 ml with distilled water. At this point, the pH of the test sample was adjusted with NaOH or HCl, and 400 µl toluidine blue solution was added. The mixture was stirred for 30 minutes and centrifuged at approximately 1,700 rpm for 20 minutes in 50-ml glass tubes in a Damon/IEC centrifuge. The supernate was decanted and brought up to 100 ml with distilled water. the sample was titrated with PVSK, using a syringe pump to feed the PVSK and a magnetic stirrer for agitation.

The titration was completely monitored by a Brinkmann Instrument dipping probe colorimeter, which was fitted with a 620-nm interference filter having a 20-nm bandpass and a stainless steel probe tip having a 4-cm light path. The results of the titration were plotted by means of a recorder attached to the dipping probe colorimeter. A new mineral sample was prepared for each charge determination.

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[4] Reference to specific equipment or trade names does not imply endorsement by the Bureau of Mines.

[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

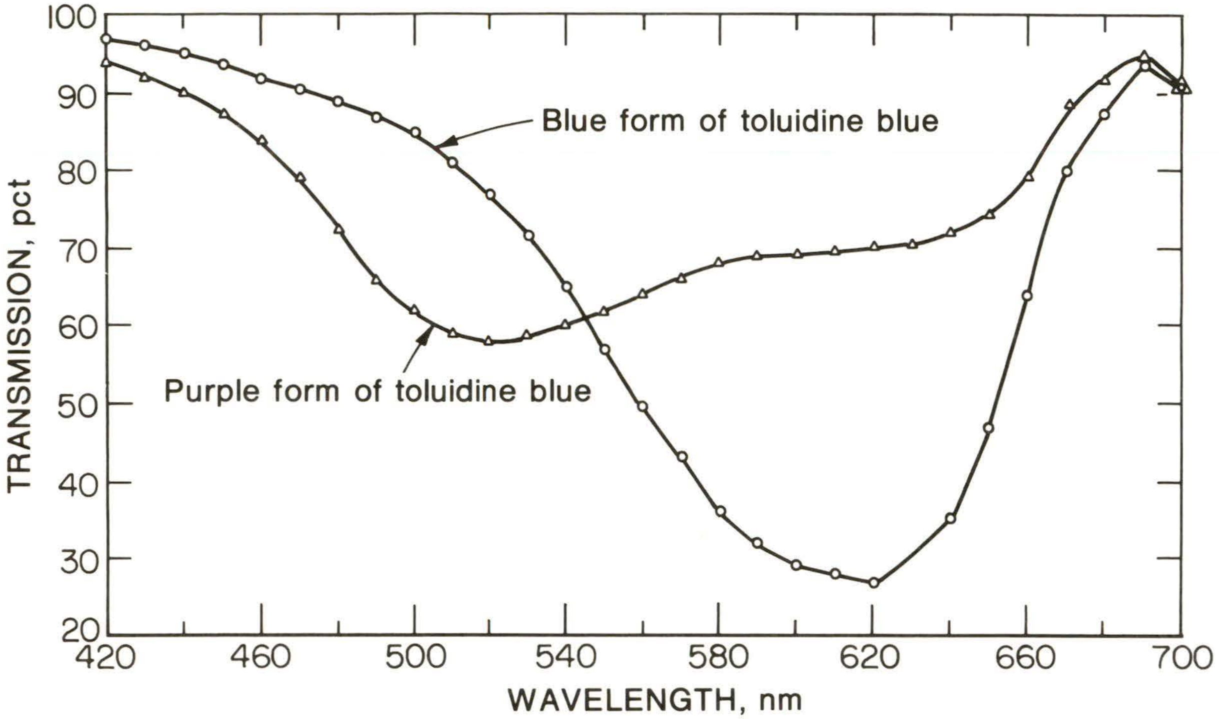

FIGURE 1. - Percent transmission of blue form and purple form of toluidine blue versus frequency.

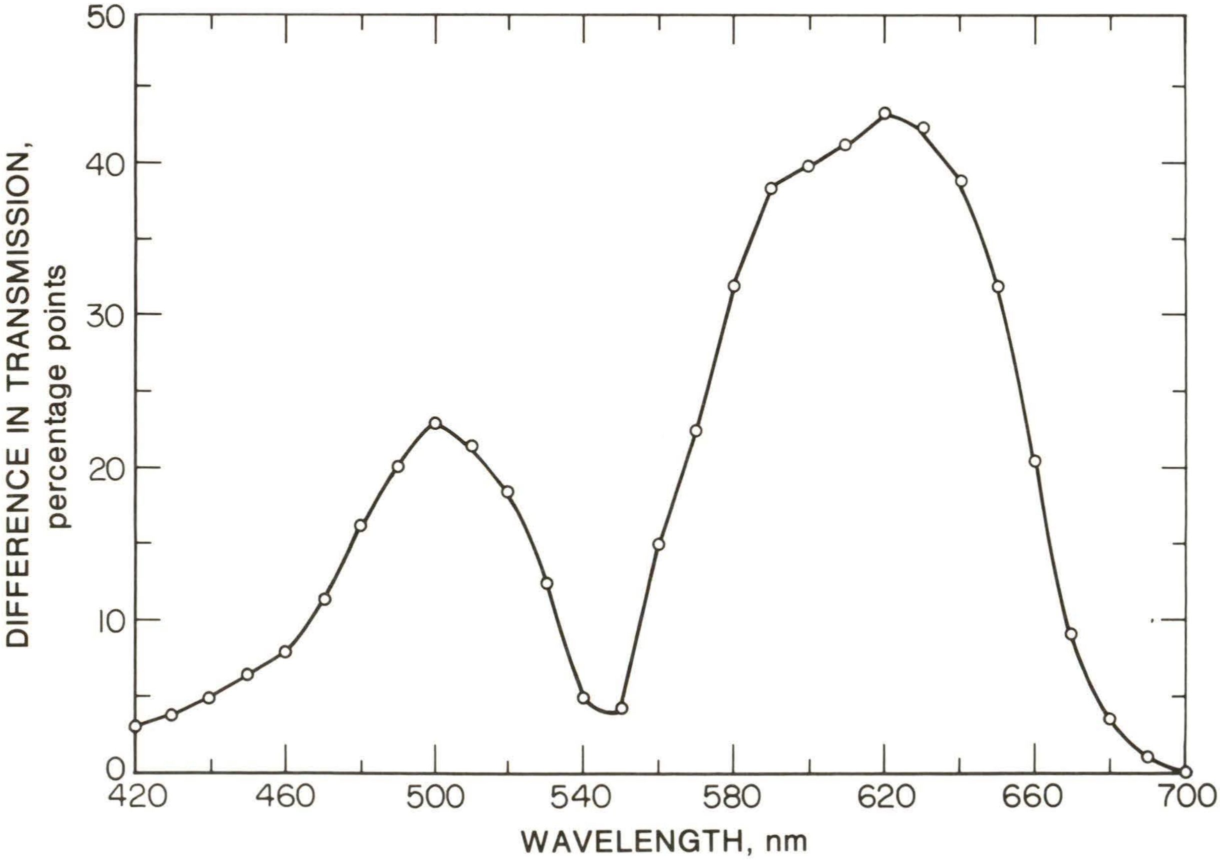

FIGURE 2. - Absolute value of difference between percent transmissions of blue form and purple form of toluidine blue.

The value of 620 nm was chosen as the wavelength for measurement by scanning a toluidine blue solution in both the blue- and purple-colored species between 340 and 740 nm with a UV-visible spectrophotometer (fig. 1). The absolute difference between the percent transmittance of the two species was plotted versus frequency as shown in figure 2. From this graph, the frequency corresponding to the maximum difference in percent transmittance between the blue and purple forms of toluidine blue was found to be 620 nm.

RESULTS AND DISCUSSION

Titrations were conducted on a variety of minerals, and the results are plotted in figures 3 and 4. A comparison of the calculated PZC values with those found in the literature is shown in table 1.

TABLE 1. - Points of zero charge for various minerals determined by titration method compared to values obtained from literature

Mineral	Value, pH		References
	Experimental	Literature	
Figure 3:			
Calcite................	9.3	9.5	2
Hematite..............	5.7	5.7	5
		5.4	4
Barite.................	5.0	4.2	8
		3.4	9
Kaolinite.............	3.2	3.4	3
Figure 4:			
Apatite................	6.4	7.0	10
Cassiterite...........	4.8	4.5	4
Celestite..............	2.3	2.3	8
Sphalerite............	1.9	2.0	1

A comparison of the values obtained by the titration method with the published values shows good agreement. In making gross comparisons such as those in table 1, it must be kept in mind that mineral compositions do vary depending on their sources. For example, apatite includes a series of minerals with differing amounts of fluoride and carbonate present. But because the values shown in table 1 are in close agreement, it appears that the titration method will give reliable PZC for various minerals.

The precision of the titration method was determined by repeating each titration five times using the same amounts of Superfloc 330 and mineral slurry. The results of one of these experiments are shown in table 2. The data indicate that the average deviation for these five titration experiments was 0.0028 ml or 1.26 pct.

TABLE 2. - Repeat titration of sample

Run	PVSK,[1] ml	Deviation from average, ml
1....................	0.221	0.001
2....................	.223	.001
3....................	.217	.005
4....................	.228	.006
5....................	.221	.001
Average........	.222	.0028

[1] The difference in the amount of PVSK needed, calculated from titrations of the mineral slurry and of the blank.

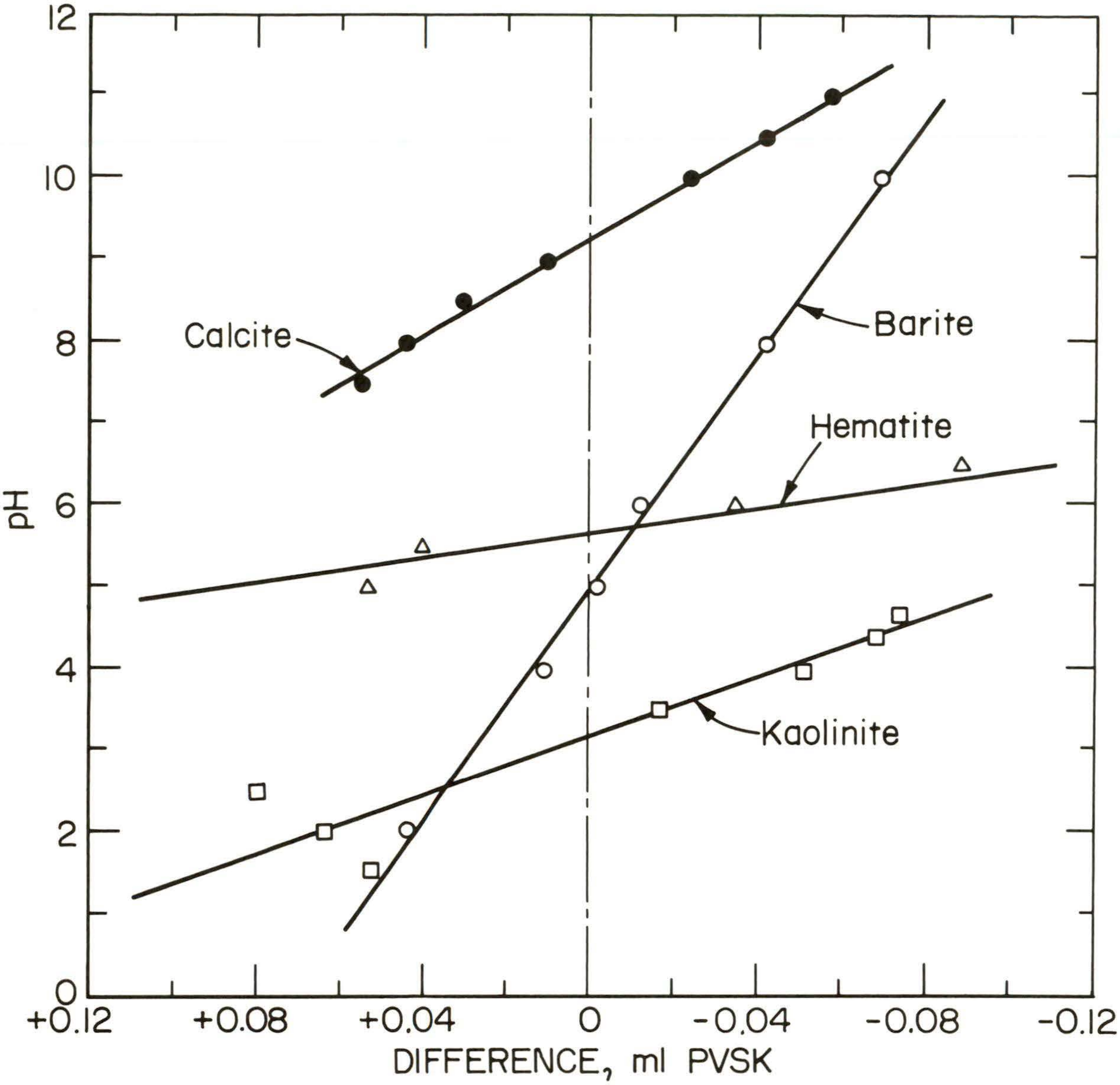

FIGURE 3. - Plot of PVSK versus pH used to determine PZC of barite, calcite, hematite, and kaolinite. The horizontal scale shows the difference between the amount of PVSK needed to titrate the mineral sample and the amount needed to titrate a blank.

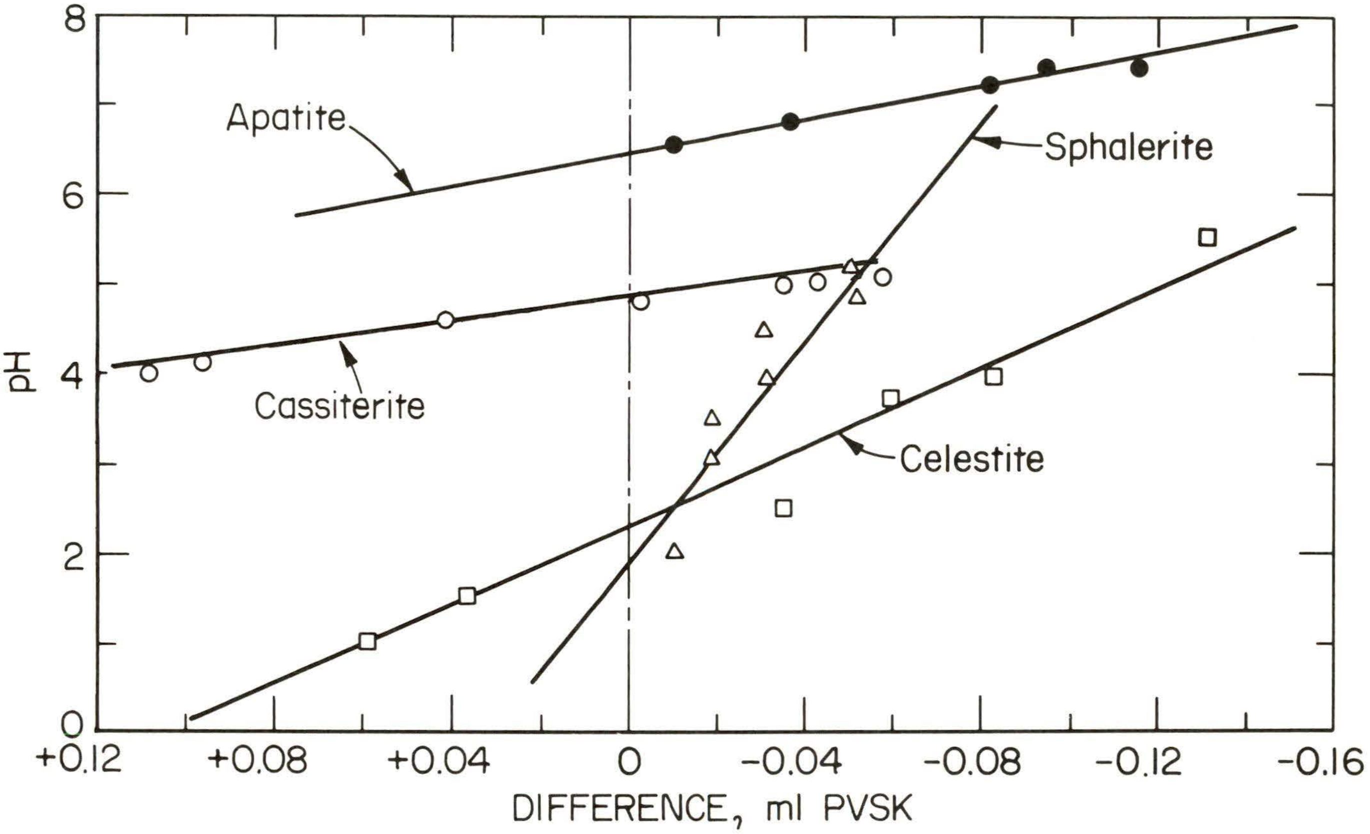

FIGURE 4. - Plot of PVSK versus pH used to determine PZC of apatite, cassiterite, celestite, and sphalerite. The horizontal scale shows the difference between the amount of PVSK needed to titrate the mineral sample and the amount needed to titrate a blank.

CONCLUSIONS

The Bureau of Mines has developed a simple technique for determining the PZC for minerals. The techniques consists of titration of the mineral with PVSK in the presence of an indicator (toluidine blue) and a positive polymer. Good agreement between PZC values obtained by the titration method and published values was obtained.

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