

KANSAS GEOLOGICAL SURVEY  
Analytical Services Section

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TURBIDIMETRIC DETERMINATION OF  $\text{SO}_4$  IN BRINES  
USING HACH REAGENTS AND THE DR/1A COLORIMETER

General Discussion:

This method is based upon the quantitative precipitation of  $\text{SO}_4$  with barium chloride. The finely divided  $\text{BaSO}_4$  turbidity formed is proportional to the amount of  $\text{SO}_4$  present in the sample. Photometric readings of light absorbance by the  $\text{BaSO}_4$  suspension is used to determine  $\text{SO}_4$  concentrations in unknowns by comparison of readings with a standard calibration curve.

Interferences:

Silica and calcium may interfere at levels above 500 mg/l and 20,000 mg/l, respectively; but chloride and magnesium do not interfere at levels up to 40,000 mg/l and 10,000 mg/l, respectively. Color or suspended material in the samples can cause high results.

Apparatus:

A Hach DR/1A colorimeter is used for the photometric measurement of standards and unknowns. The wavelength filter wheel is set to 450 nm and the %T-Abs scale is inserted into the meter.

Matched pairs of 25 ml sample cells are used in this procedure. Initially, cells of a matched pair should be cleaned, filled with distilled water, and checked for positioning in the cell holder which yields comparable absorbance readings for both cells. These positions of the cells in the holder are noted by the placement of a dot on the neck of each cell on the side nearest to the wavelength filter wheel. An "R" is also placed on the neck of one of the cells of the matched pair. This cell will be used with the untreated portions of the samples which serve as reference solutions in this method.

Reagents:

Hach powder-pillows of Sulfa-Ver-4 reagent for a 25 ml sample size are used for the formation of the  $\text{BaSO}_4$  suspensions.

### Calibration Standards:

Working standards for a calibration curve are prepared from a 1000 mg  $\text{SO}_4$ /l sodium sulfate stock solution (1.47865 g  $\text{Na}_2\text{SO}_4$ /l). Appropriate volumes of the stock solution are pipeted into 50 ml volumetric flasks, diluted to the mark with distilled water, and mixed thoroughly. The volumes of stock solution needed for the preparation of the calibration standards in 50 ml volumetric flasks are:

<u>ml of 1000 mg <math>\text{SO}_4</math>/l stock</u>	<u>mg <math>\text{SO}_4</math>/l</u>
3.0	60
2.0	40
1.0	20

### Operating Notes:

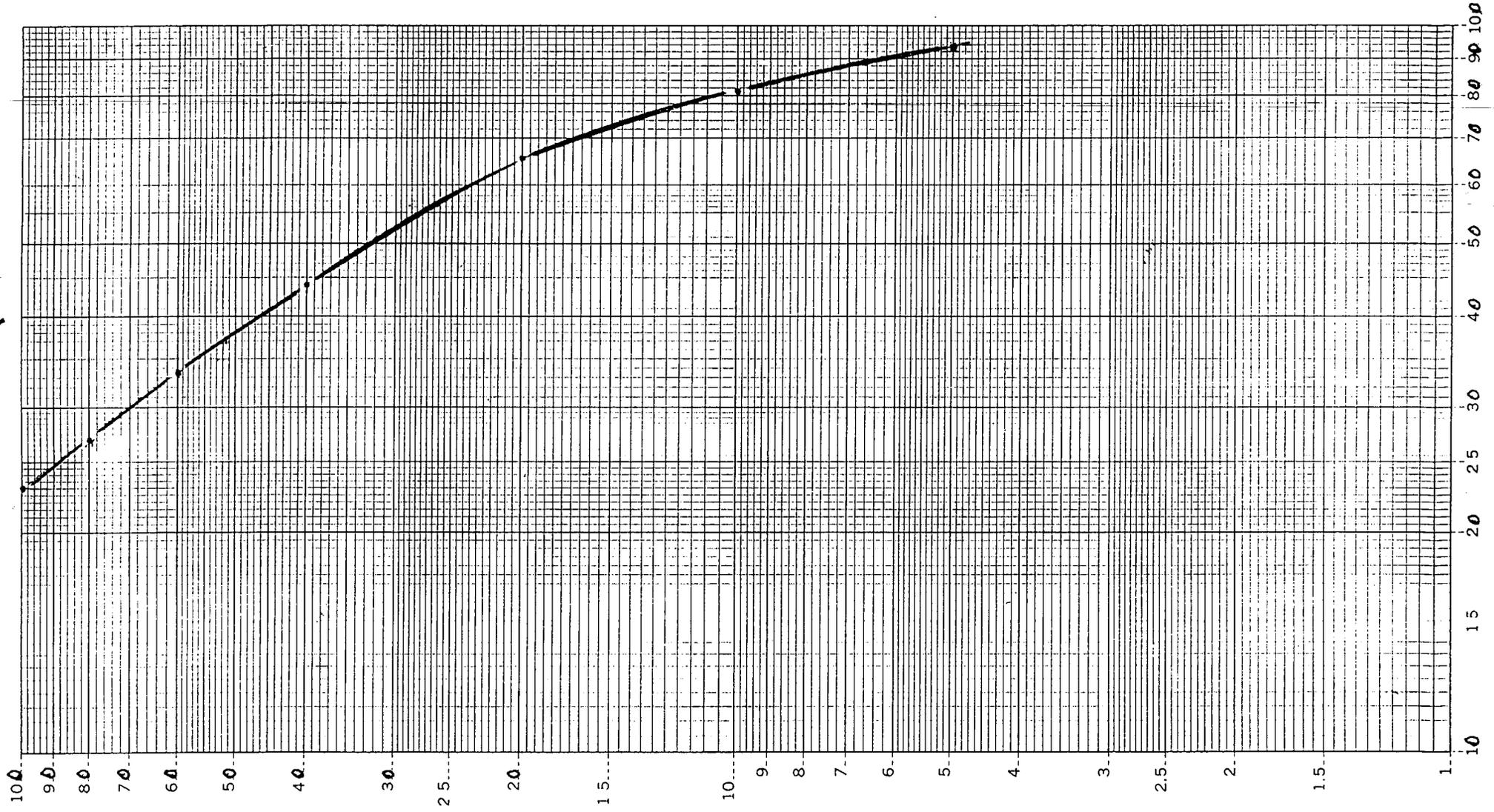
1. A 20-60 mg  $\text{SO}_4$ /l operating range has been adopted for the application of this method to  $\text{SO}_4$  determination in brines. If the  $\text{SO}_4$  concentration is above this range, a dilution of the original sample should be made using distilled water as the diluent. The reference solution for the diluted brine sample should be the diluted sample itself. If  $\text{SO}_4$  levels are below 20 mg/l, additional standards of 5 mg/l and 10 mg/l may be added to produce an extended calibration curve. Standards below 5 mg/l do not fall on an extrapolation of the 20-60 mg/l curve.
2. Turn the power switch to the LEFT SET position and allow the meter response to stabilize. Use the LEFT SET CONTROL to adjust the meter to 0% T.
3. Place an untreated portion of the sample into the cell marked with an "R" on its neck. This is the reference solution which is used to set the 100% T on the colorimeter just prior to making an absorbance reading on the treated portion of the sample. The reference solution is distilled water in the case of the calibration standards and is an untreated portion of the solution being analyzed in the case of unknowns. The use of an untreated portion of the unknown solution as the reference solution serves to compensate for the presence of color or suspended material.
4. Place 25 ml of the sample into the other cell of the matched set. Add the contents of a Sulfa-Ver-4 powder-pillow, swirl for 30 seconds to dissolve the reagent, and then allow the sample to stand undisturbed for 5 minutes while the  $\text{BaSO}_4$  suspension continues to develop.

5. About 1 minute before the development period is up, place the cell containing the untreated reference solution into the colorimeter with the dot on its neck facing toward the wavelength filter wheel. Close the cell holder lid, switch the power knob to ON, and use the RIGHT SET CONTROL to adjust the meter to 100% T. It may take a few seconds for the meter response to stabilize.
6. At the end of the 5 minute development period remove the reference sample cell and insert the cell containing the treated sample, black dot toward the filter wheel. Allow the meter to stabilize and then record the % T reading.
7. Repeat steps 2-6 for each new standard or unknown solution. After proper warm-up the 0% T reading should be fairly stable from sample to sample, but the 100% T may need adjustment. The cell used with the Sulfs-Ver-4 treated samples should be swabbed with a cotton Q-tip and rinsed with distilled water in between samples. Rinse the cell with some of the next sample to be run before filling the cell again. This procedure will minimize errors associated with the build-up of a  $\text{BaSO}_4$  film on the cell walls.
8. A parabolic curve fitting routine using  $\log \% T$  vs  $\log \text{mg/l}$  is applied to the data of the standards in order to evaluate  $\text{SO}_4$  concentrations from the % T data of the unknowns. The ease of reading the linear % T scale and the use of the parabolic curve fitting routine for the  $\log \% T$  vs  $\log \text{mg/l}$  plot of the calibration standards data provide greater accuracy than is possible from the logarithmic concentration scale provided with the DR/1A colorimeter for the  $\text{SO}_4$  Sulfa-Ver-4 method. The present method also overcomes the problem of any variation in laboratory environmental conditions under which the unknowns have run as compared to those which existed during the accumulation of data used to produce the Sulfa-Ver-4  $\text{SO}_4$  scale.

References:

1. Hach Company, 1989, Sulfate, Photometric Determination: In Water Analysis Handbook, G. L. Walters, editor, Hach Company, Loveland, CO, pp. 567-571, 656.
2. APHA, AWWA, and WPCF, 1985, Sulfate 426C. Turbidimetric Method: In Standard Methods for the Examination of Water and Wastewater, 16 th ed., APHA Pub., Washington, D.C., pp. 467-468.

CALIBRATION CURVE FOR THE TURBIDIMETRIC  $SO_4$  METHOD



$SO_4$  mg/l