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TECHNICAL ARTICLE

Development and Validation of a Spectrophotometric Method to Measure Sulfate Concentrations in Mine Water without Interference

Arup Roy · Bidus Kanti Das · Jayanta Bhattacharya

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Abstract Sulfate concentrations are determined in mine water by gravimetric, titrimetric, colorimetric, turbidometric, ion chromatographic, inductively coupled plasma absorption spectrophotometric, and other methods. Accurate sulfate measurement of mine water can be difficult due to interfering groups, cations, and anions, mainly arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}). In this paper, a simple and effective spectrophotometric method is described for the determination of sulfate in mine water. When the SO_4^{2-} reacts with barium chloranilate at pH 4.5 in aqueous ethyl alcohol solution, it releases acid-chloranilate, which shows maximum absorption at 350 nm and obeys Beer's law over the concentration range of 10–1,000 mg/L. Results show that the proposed method was significantly more accurate than a conventional method. Absorbance was found to increase linearly with increasing concentration of sulfate, which is corroborated by the calculated correlation coefficient value of 0.999 ($n = 7$). The slope and intercept of the equation of the regression line were 0.00091 and 0.00778, respectively. The limit of detection and limit of quantification were found to be 0.03861 and 0.06774 mg/L, respectively. The validity of the described procedure was assessed. Statistical analysis of the result indicated high accuracy and good precision. The proposed method was successfully applied in mine water without interference from common groups like AsO_4^{3-} and PO_4^{3-}. The relative standard deviations of the proposed method ranged from 0.03 to 0.26%, with recoveries of 99.79–101.57%.

Keywords Interference · Mine water · Spectroscopy · Sulfate · Validation

Introduction

Sulfate ions are commonly found in natural ground and surface waters. Acid mine drainage (AMD), generated mostly by pyrite oxidation at mine sites, contain significant concentrations of heavy metal cations and anions such as sulfate, phosphate, arsenate, carbonate, chloride, and nitrate (Johnson 2003). Performance of AMD treatment technologies using sulfate-reducing bioreactors are evaluated based on the concentration of residual sulfate (Bhattacharya 2008; Kolmert et al. 2000). The US Code of Federal Regulations specifies that sulfate should not exceed 250 mg/L in drinking water (USCFR 1979).

Many direct and indirect methods are used to measure sulfate ions in mine water, including ion chromatography (IC) (Kaksonen et al. 2003; Morales et al. 2000), inductively coupled plasma absorption spectrophotometry (ICP-AES) (Christensen et al. 1996), turbidimetric (Elenkova et al. 1980; Raghavan and Raha 1991), colorimetric (Bertolacini and Barney 1957), titrimetric (Budesinsky and KrumLova 1967), spectrophotometric (Davis and Lindstrom 1972), and gravimetric methods (APHA 1985).

The classic gravimetric technique, in which precipitation as barium sulphate is employed, is time-consuming and subject to errors caused by coprecipitation of Ca^{2+} and Mg^{2+} (DESCA 1980). Titrimetric methods in ethanolic solution with thorin as an indicator have been described (Fritz and Yamamura 1955; Macchi et al. 1969), but the conditions necessary for satisfactory titrations are critical for accuracy (Haartz et al. 1979) and prior removal of cations from the

A. Roy · B. K. Das · J. Bhattacharya (✉)
Department of Mining Engineering, Indian Institute of Technology, Kharagpur 721302, India
e-mail: jayantaism@gmail.com

sample by ion exchange (Fritz and Yamamura 1955) is required.

Automated spectrophotometric techniques (Adamski and Villard 1975; Persson 1966) can provide fairly rapid sample throughput combined with reasonable precision, but cations interfere with the colorimetric method by forming insoluble chloranilates (Miles and Cook 1982; Reisman et al. 2007). Also, even small amounts (e.g. 10 ppm) of phosphate and arsenate can cause interference because they have higher optical density (O.D) than sulfate and because barium salts of those anions are also insoluble in water (Iwasaki et al. 1957). Cation exchange resin can be used to convert typical interfering anions, such as arsenate, phosphate, chloride, nitrate, and carbonate ions, to free acids, such as hydrochloric, nitric, and carbonic acids. These acids are conveniently evaporated by heating the solution in a Teflon beaker at 160°C (Kamaya et al. 1993).

Sulfate concentration can be measured directly using ion chromatography. Anions present in the sample are separated on the basis of their relative affinities and detected by measuring suppressed conductivity. For the measurement of sulfate from mine drainage or treated mine acidic water, acid extraction with HCl is essential (Johnson 1955). However, authors of a review (Singh et al. 1996) on suppressed ion chromatographic analysis of anions in environmental waters cautioned that measurement of low levels of sulfate should be validated by other well-established methods.

Another method of sulfate measurement is the turbidimetric method, which is based on precipitation of sulfate ions as insoluble barium sulfates (Morais et al. 2003; Sheen et al. 1935; Singh et al. 1996; Sobek et al. 1978). The stability of barium sulfate is the main concern with this method. To improve the stability of the barium sulfate suspension, different stabilizing agents, including thymol and gelatin, tween80 (polysorbate 80), and polyvinyl alcohol, are employed (Sheen et al. 1935; Singh et al. 1996). Baban et al. (1980) used EDTA in the barium sulfate turbidimetric method to reduce interference by metal ions. The turbidimetric sulfate determination method, however, is limited by its quantification range, and is subject to interference by nitrate, phosphate, arsenate, and bicarbonate ions (Burakham et al. 2004).

The use of ICP-AES is an indirect method for sulfate measurement in water containing interfering agents. However, the ICP-AES actually measures the concentration of sulfur, not sulfate. ICP-AES sulfate measurement has not been widely used in mine water analysis because of the typically high concentrations of sulfate and significant quantities of sulfide and sulfite (Burakham et al. 2004). In addition, calcium and hydrochloric acid can cause interference during ICP-AES quantification (von Staden and Taljaard 1996).

In the spectrophotometric method, sulfate is measured by the addition of barium chloranilate, which reacts with sulfate ions to liberate chloranilic acid. Sulfate concentration is measured in terms of UV absorption by chloranilic acid at a specific wavelength. According to Beer's law, optical density depends on the concentration of liberated chloranilic acid, which may be influenced by interfering groups, such as arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}), even at concentrations less than 10 ppm, since they also liberate chloranic acid, resulting in a higher optical density. For this paper, we describe a method in which these two interfering anions are eliminated prior to spectrophotometric measurement of sulfate. In the absence of interfering groups, the chloranilic acid produced by the reaction between sulfate and barium chloranilate produces a more accurate optical density.

Materials and Methods

Apparatus

The spectrophotometric measurements were carried out using a Shimadzu model 1800 UVVIS spectrophotometer with a diode array detector (DAD) (range 190–1,100 nm). The UV spectra of standard and sample solutions were recorded in 1 cm quartz cells at a wavelength of 530 nm. Statistical analysis was performed using SPSS (Version 10.7) and EffiValidation 3.0 software.

Reagents and Solutions

Stock sulfate solution of 1,000 mg/L was prepared by adding 1.479 g of dried sodium sulfate (Na_2SO_4) to deionized water (18 mΩ/cm), and diluting it to 1 L. This was kept in the dark at a maximum temperature of 4°C for, at most, 1 month. Working standard solutions were prepared daily by diluting stock solution. Barium chloranilate ($BaC_6Cl_2O_4$) stock solutions were created by adding 9 g to 333 mL of spectrophotometric grade ethyl alcohol and diluting it to 1 L with deionized water. Ammonium molybdate reagent was prepared by dissolving 45 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in a mixture of 70 mL of 25% ammonium solution and 140 mL of water. The ammonium molybdate was then mixed with a solution of 250 mL of concentrated nitric acid and 500 mL of water. The whole solution was diluted to 1 L and kept in brown bottle and allowed to stand for 1–2 days. Acetate buffer of pH 4.5 was prepared by mixing 13.6 g of sodium acetate and 6.4 mL of acetic acid in a 1 L volumetric flask and then adding deionized water up to the mark. All chemicals were procured from Merck, Germany. Dowex-50W-X8 ionic form-H^+, 20–50 mesh size was procured from Fluka analytical, USA and used as the ion exchange resin. The column was prepared by pouring the resin into a 55 cm × 1 cm inner diameter glass econo-column. The column, when exhausted, turns red. The column was packed carefully to ensure that air pockets were not present in the column.

Calibration Curve Procedure

A set of different concentrations of sulfate solutions of 10, 50, 100, 250, 500, 750, and 1,000 mg/L were prepared using the stock solution. Samples for each test were prepared by adding 9.37 mg of Na_2HAsO_4 and 9.45 mg of K_2HPO_4 to 25 mL of freshly prepared standard sulfate solutions, so that the concentrations of PO_4^{3-} and AsO_4^{3-} were 250 mg/L in each standard solution. After thorough mixing, those standard solutions were used to prepare a standard calibration curve; 25 mL of each standard sulfate solution was passed through the 55 cm × 1 cm column, which was packed with the Dowex-50W-X8 resin. The upper part of the column was packed with glass wool. Using gravity, the sample was collected in the Erlenmeyer flask at the end of the column. Thereafter, the samples were treated with 10 mL of ammonium molybdate reagent, phosphate (PO_4^{3-}), and arsenate (AsO_4^{3-}), resulting in the precipitation of phosphomolybdate and arsenomolybdate, respectively (Atkins and Edith 1926; Barrer et al. 2002). The precipitate was removed by filtration using 0.45 μm membrane filters. In the final step, 2 mL of sample were added to a test tube to which 8 mL of ethanol was added. A portion (8 mL) of ethanolic sulfate solution was withdrawn into a centrifuge tube and mixed with 2 mL of acetate buffer (pH 4.5) solution and reacted with 5 mL of barium chloranilate solution. The mixture was shaken for 10 min. The resultant reaction is given in Eq. (1).

$$SO_4^{2-} + BaC_6Cl_2O_4 + H^+ = HC_6Cl_2O_4 + BaSO_4\downarrow \quad (1)$$

Excess barium chloranilate and precipitated barium sulfate were removed by centrifugation at 8,000 rpm for 5 min. Blank solutions were prepared by the same process using deionized water instead of sulfate solution. The supernatants were analyzed spectrophotometrically. In aqueous ethyl alcohol solutions at pH 4.5, a well-defined peak of chloranilate was obtained with maximum absorbance at a wavelength of 350 nm (Fig. 1).

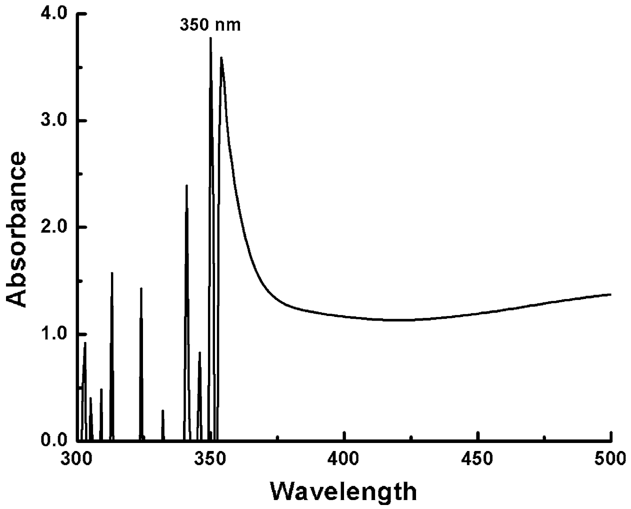

Fig. 1 UV spectrum of chloranilate in aqueous ethanol solution

Results and Discussion

Paired *t* Test

We compared our method of sulfate determination to an existing standard turbidimetric method (US EPA 1979) commonly used for sulfate analyses. We used SPSS software to conduct a paired *t* test to find out if there was any significant difference in between these two methods. The results (Table 1) are based on sulfate concentration as the independent variable and optical density as the resultant variable, using the two different analytical methods as dependent variables. The critical t value was based on an α (critical value) value of 0.05 (95% confidence limit). Here $t_{(0.05,\ 6)}$ means to determine the 0.05 critical value from the t distribution with 6 degrees of freedom.

A statistically calculated "t" value equal to $t_{(0.05,\ 6)}$ would indicate that there is no significant difference between the two methods. However, if t is greater than $t_{(0.05,\ 6)}$ ($t > t_{(0.05,\ 6)}$), then our method is more accurate for measuring sulfate concentrations in water than the existing spectrophotometric method. We calculated a t value of 4.800 from our comparison of results. This t value clearly exceeds $t_{(0.05,\ 6)} = 2.447$ from the *t*-test table. There was a significant difference in the mean scores of the two methods, $t = 4.80(6)$, $\alpha < 0.05$. The regression (R^2) values in Fig. 2 and Fig. 3 suggest that there was a significant difference between the existing standard method and our proposed spectrophotometric method. This difference is attributed to the elimination of interfering groups. Optical density depends on the concentration of liberated chloranilic acid, which is influenced by interfering groups. In our method, there was no influence by interfering groups, so a more accurate optical density resulted.

Validation

Validation is one of the most important steps in method development for analytical determinations. The main validation parameters, stability, linearity, sensitivity, precision, accuracy, recovery, and specificity, were evaluated for our method (EAEMP 1996; Green 1996). All the validation parameters were analyzed using standard solutions.

Table 1 Paired *t*-test results between the existing (Ex) and proposed (Pr) methods using SPSS software and paired samples statistics

	Mean	N	Standard deviation	Standard error (mean)
Pair 1				
Ex	0.456	7	0.363	0.137
Pr	0.365	7	0.335	0.126

		Correlation	Significance
Pair 1			
Ex and Pr	7	0.99	0.00

	Mean	Std. deviation	Std. error (mean)	95% confidence interval of the difference		t	*df*[a]	Sig.[b]
				Lower	Upper			
Pair 1								
Ex-Pr	0.091	0.050	0.018	0.044	0.137	4.800	6	0.003

[a] *df* degrees of freedom

[b] *Sig.* significance of 2-tailed *t* test

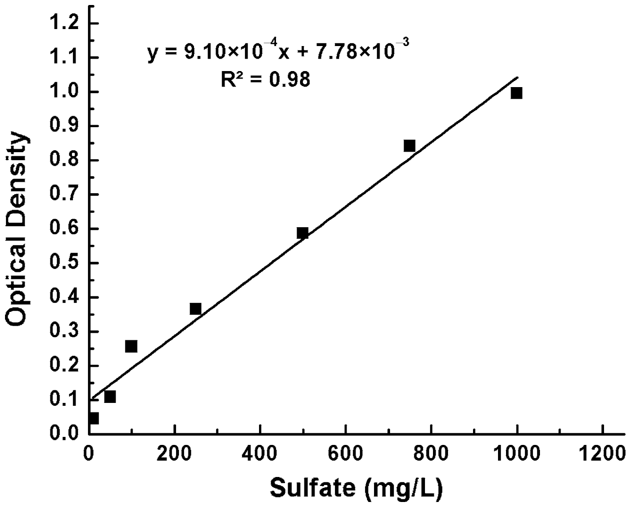

Fig. 2 Regression analysis of the calibration curve of sulfate showed a linear relationship between the intensity of absorbance and the concentration, with a correlation coefficient using an existing method

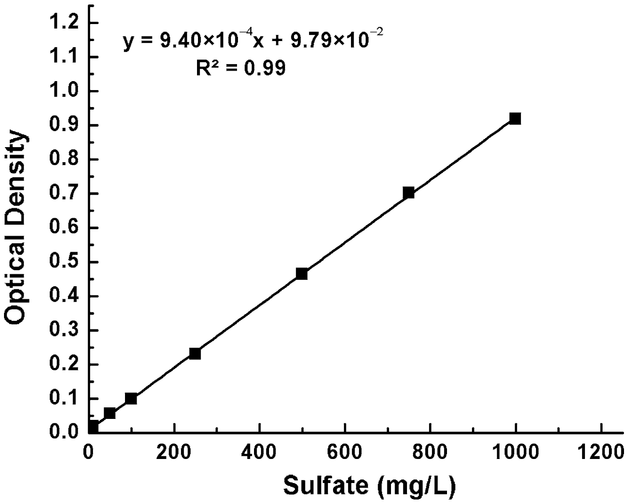

Fig. 3 Regression analysis of the calibration curve of sulfate shows a linear relationship between the intensity of absorbance and the concentration, with a correlation coefficient using the proposed method

Stability

The standard stock solutions of sulfate were stored at +4°C for 1 month. Then, the solutions were analyzed with our UV spectrophotometric method. The spectrum was compared with the spectrum of daily prepared standard solution and no difference was observed in them.

Linearity Range

Under the experimental conditions, the calibration graphs of the absorbance versus the concentration were found to be linear over the range of 10–1,000 mg/mL for our method. The calibration graphs in Fig. 2 were constructed after analyses of 7 different concentrations, with each concentration measured 10 times. Each point of the calibration graph corresponded to a mean value obtained from 7 independent measurements. The regression equations (with standard error of intercept and slope) and correlation coefficients of the mean of 7 consecutive calibration curves are given in Table 2. The regression equation was $y = 0.00091x + 0.00778$, where y is the absorbance and x is the concentration in mg/L ($r = 0.99991$).

Table 2 Regression data of the calibration line for quantitative determination of sulfate by proposed method

Parameters	Sulfate
Measured wavelength (λmax), nm	350
Linearity range, mg/L	10–1,000
Regression equation	$y = 9.10 \times 10^{-4x} + 7.78 \times 10^{-3}$
Slope	9.10×10^{-4}
Slope standard deviation	1.00×10^{-5}
Intercept	7.78×10^{-3}
Intercept standard deviation	2.91×10^{-3}
Correlation coefficient (r)	0.99
QC coefficient	1.35
Limit of detection, LOD, mg/L	3.86×10^{-2}
Limit of quantification, LOQ, mg/L	6.77×10^{-2}
Sensitivity of the proposed method	9.10×10^{-4}
Repeatability of the proposed method	2.23×10^{-3}
Reproducibility of the proposed method	8.70×10^{-2}

Limits of Detection and Quantification

The Limit of Detection (LOD) and Limit of Quantification (LOQ) for sulfate were determined by the proposed method using calibrated sample standards. The LOD and LOQ were calculated as 3.3 σ/S and 10 σ/S, respectively, where S is the slope of the calibration curve and σ is the standard deviation of the y-intercept of the regression equation (n = 5) (Table 2).

Precision

The precision of a method is defined as the closeness of agreement between independent test results obtained under optimum conditions. Four different concentrations of sulfate in the linear range (80, 160, 400, and 950 mg/L) were analyzed in 8 independent series on the same day (intra-day precision) and 3 consecutive days (inter-day precision) from 4 measurements of every sample in each series. The precision of the analysis was determined by calculating the relative standard deviation (%R.S.D.). The R.S.D. values of intra-day and inter-day studies varied from 0.0047 to 0.4054%, showing that the intermediate precision of the method was satisfactory (Table 3).

Table 4 The result of percentage recovery value for proposed method (n = 5); concentrations in mg/L

Sulfate in mine water	Standard sulfate added	Total sulfate observed (±S.D.)	% recovery (±R.S.D.)
356	0	356.02 ± 0.09	100.10 ± 0.03
356	20	376.11 ± 0.05	100.57 ± 0.26
356	70	425.86 ± 0.06	99.79 ± 0.09
356	150	505.95 ± 0.07	99.96 ± 0.05

Accuracy and Recovery

The accuracy of the method was determined by calculating the percentage of relative error (bias %) between the mean measured concentrations, after addition of standards with the same concentration of sulfate. The results obtained for intra and inter-day accuracy were between −0.04 and 0.35 (Table 3). Observed concentration values agreed well with the standards. To provide additional support to the accuracy of the proposed method, a standard addition method was employed. One mine water sample (Charcha mine) was analyzed (n = 5) by this method and the sulfate concentration in this mine water was found to be 356 mg/L. Three different concentrations of standard sulfate solution (20, 70, 150 mg/L) were added and the total concentration was determined using the proposed method (n = 5). The percent recovery of the added standard sulfate was calculated as percent recovery = $[(C_t–C_s)/C_a] \times 100$, where C_t, is the total sulfate concentration measured after standard addition, C_s, sulfate concentration in the mine water sample and C_a, sulfate concentration added to mine water sample (Table 4). The mean percent recoveries (% R.S.D.) for the intermediate concentration were found to be 100.57 (0.26), 99.80 (0.09) and 99.96 (0.05), respectively. These results revealed that any small change in the sulfate concentration in the solutions could be accurately determined by the proposed method.

Table 3 Precision and accuracy data of the proposed spectrophotometric method for the analysis of sulfate (n = 5)

Added mg/L	Inter-day observed[a] mg/L	Intra-day precision% R.S.D.	Accuracy[b] bias %	Observed[a] mg/L	Precision% R.S.D.	Accuracy[b] bias %
30	30.02 ± 0.12	0.40	0.07	30.10 ± 0.09	0.30	0.35
80	80.01 ± 0.10	0.12	0.01	80.03 ± 0.09	0.10	0.04
160	160.05 ± 0.10	0.06	0.03	159.93 ± 0.05	0.03	−0.04
400	399.94 ± 0.11	0.02	−0.01	400.11 ± 0.10	0.02	0.02
950	950.18 ± 0.04	0.00	0.01	949.86 ± 0.11	0.00	−0.01

[a] Observed = mean ± standard deviation; % R.S.D. = relative standard deviation

[b] Accuracy = [(observed–added)] × 100

Conclusion

The study reports a useful and reliable UV spectrophotometric method that we have developed and validated for the routine determination of sulfate in mine water. The method was found to be suitable for precise and accurate determinations of sulfate concentrations over the range of 10–1,000 mg/L. The limits of detection and quantification for sulfate at lower concentrations were 0.039 and 0.068 mg/L, respectively. From the results obtained, we conclude that the method has high sensitivity, accuracy, reproducibility, and specificity.

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