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Article

Accurately Determining Groundwater Sulfate Concentrations from Reclaimed Landscapes with Conductometric Titrations

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Cite This: *ACS EST Water* 2023, 3, 2544−2550

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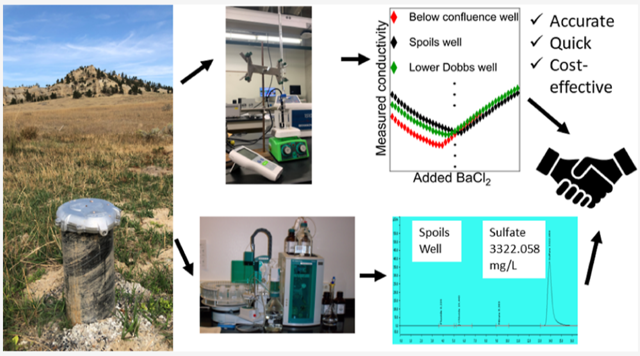
ABSTRACT: Conductometric titrations were used to measure sulfate concentrations in ground and surface water samples taken from land reclaimed after open-air coal mining. Sulfate concentrations ranged from 460 mg/L in surface water upstream of the former coal mine's location to almost 3500 mg/L in groundwater sampled at the spoil site. Data from the titration measurements were benchmarked against EPA-approved ion chromatography (IC) measurements and results agreed to within ±3.6% (averaged over 36 samples) with a range of +10.4 and −11.3%. To test the generality of conductometric titration as a method for measuring dissolved constituents in environmental aquatic systems, additional measurements testing for chloride were performed with surface water samples collected from four different sites in south central and southwest Montana. Chloride concentrations ranged from 2.2 to 12 ppm. Based on measurements with control samples prepared in the laboratory, the environmental sample measurements are believed to be accurate to within ±6.4%. These conductometric titration studies highlight the technique's simplicity, accuracy, cost effectiveness, and potential to produce rapid results. Additional analyses suggest that even simpler, non-species-specific conductivity data can provide an on-site, rapid assessment of sulfate levels in ground and surface water when historical speciation data are available.



KEYWORDS: *sulfate, groundwater contamination, conductometric titration, reclamation, salinity, coal mine reclamation*

INTRODUCTION

Ground and surface water salinity is a growing threat to ecosystems and human health.[1−7] As the salinity increases, especially in rural areas that rely on ground and surface water for personal and agricultural needs, individuals and communities increasingly require fast, accurate methods for assessing not only how much salt is in the water but also salt speciation. Depending on the analyte of interest, analytical laboratories remote from the sampling site(s) will use different EPA-approved techniques such as atomic emission spectroscopy, mass spectrometry, ion chromatography, and colorimetry to identify and quantify water contaminants.[8−11] While these processes lead to accurate, validated data, the measurements themselves require careful handling and transport of field samples and often require additional processing before results are acquired. The time between collecting a sample in the field and having results in hand can be weeks, and the cost of these analyses is often prohibitive to end users who must determine if water is safe for use.

In many instances, however, end users will need to know in real time if available water is not suitable for its intended use. One contaminant requiring rapid and accurate assessment in the central and mountain west regions of the United States is sulfate.[12] Even though there is no federally enforceable regulatory limit for sulfate concentrations, sulfate has a secondary maximum contaminant level of 250 mg/L in drinking water provided by the EPA.[13] High sulfate concentrations are known to adversely affect people if concentrations rise above 500 mg/L.[14] In addition, sulfate concentrations above 2500 mg/L result in weight loss and health problems in cattle, and cattle begin to suffer neurological disorders when sulfate concentrations rise above 3000 mg/L.[14] Finally, sulfate salts in soil create an imbalance of adsorbed ions in sensitive crops by limiting calcium uptake while promoting potassium and sodium uptake.[15]

Sulfate concentrations exceeding the human and/or cattle health standard levels are common in the Powder River Basin (PRB) in Montana and Wyoming.[16] This region is home to some of the largest open-air coal mines in the world.[17] The large-scale disruption to local landscapes resulting from mining activities alters groundwater composition. In the PRB, these

Received: March 17, 2023
Revised: July 5, 2023
Accepted: July 6, 2023
Published: July 20, 2023

https://doi.org/10.1021/acsestwater.3c00126
ACS EST Water 2023, 3, 2544−2550

disruptions create greater access to soluble gypsum ($CaSO_4\cdot 2H_2O$) in evaporites, leading to unacceptable high sulfate concentrations.[18−20] Data in Figure 1 show sulfate concentrations in more than 1000 wells located throughout the PRB in Montana. These compiled results show that sulfate levels in tertiary and quaternary aquifers consistently exceed the EPA secondary limits by wide margins. Degraded water quality impacts local agriculture and ranching in the PRB, meaning that farmers and ranchers must regularly evaluate water from wells and streams to ensure it is suitable for irrigation and for livestock. Given the seasonal variability in ground and surface water flow and long-term changes in water tables and groundwater composition, this water quality testing is necessary to ensure human, animal, and ecosystem health.

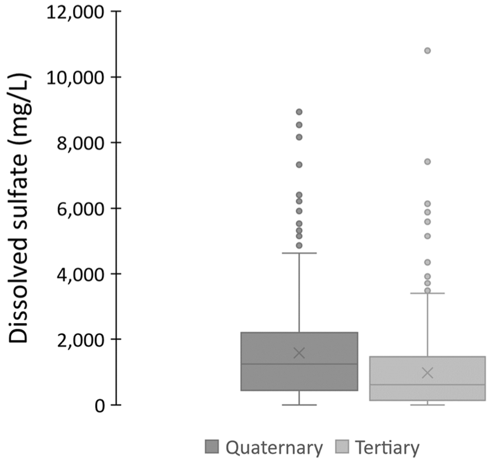


Figure 1. Sulfate concentrations in quaternary (n = 369) and tertiary (n = 636) aged aquifers in Rosebud and Big Horn Counties, including alluvium, spoils, and sandstone aquifers. The box plot represents the minimum and maximum (vertical lines), the first and third quartile (box), the median and mean (horizontal lines and x), and outliers (values that exceed 1.5 times the interquartile range; points) of the publicly available geochemistry for these counties. Average sulfate concentrations found in the quaternary and tertiary aged aquifers are 1588 and 982 mg/L, respectively.[16]

Studies described in this work develop and apply conductometric titration methods to quantify the amount of sulfate in groundwater samples collected from a reclaimed open-air coal mine site in southeast Montana. The mine itself operated from 1969 to 2003, and land-surface reclamation began at that time when operation ceased. In 2022, the first of several phase IV bonds was released when the reclamation process was completed and the land returned to private ownership. Sulfate concentrations are measured in samples taken from 12 sites (8 groundwater and 4 surface water) on three separate occasions at and surrounding reclaimed land overlaying the original spoil pile of this former open-air coal mining site. Conductometric titration measurements performed with these samples demonstrate this method's utility as a rapid and accurate tool for evaluating sulfate concentrations. Conductometric titration data are compared to concentrations determined from independent ion chromatography measurements performed using split samples. The agreement between the two measurements is quite good, with an average difference of ±3.6% for a given sample. To test the generality of conductometric titration as a tool for assessing ion concentrations in environmental systems, we also use this technique to measure chloride concentrations in several rivers and streams in south central and southwest Montana. These results are also validated by comparing them with data from independent ion chromatography analyses and reinforce the notion that this simple, inexpensive technique can be a useful tool for rapid, accurate water quality assessment.

■ MATERIALS AND METHODS

Proof of Principle (SO_4^{2-} Analysis). Conductometric titration has been used previously to analyze different analyte concentrations.[21,22] While the analyte and titrant will vary depending on the intended application, the technique's principle is the same: for the given (charged) analyte of interest, a suitable complexation agent is titrated into the solution, and the conductivity is measured. As the analyte and agent precipitate, the solution's conductivity diminishes until the analyte has been removed from the solution. The addition of titrant past the endpoint results in the solution's conductivity rising. From the minimum in the conductivity vs titrant added data, one can readily calculate how much of the analyte was in the original solution.

Even though conductometric titration is more commonly used to analyze acids and bases as an alternative to pH titrations, its potential for sulfate analysis was investigated and proven successful by Garcia and Schultz in an undergraduate laboratory experiment,[23] as well as for laboratory-controlled gypsum dissolution experiments.[24] This technique, however, has not been previously adapted to examine chemically complex aqueous solutions having high ionic strengths, and, to our knowledge, data from conductometric titration experiments have not been benchmarked against more conventional analytical techniques traditionally used to assess groundwater quality.

For experiments performed in this study, ground and surface water samples believed to have high sulfate concentrations are titrated with 8.6 mM $BaCl_2$. $BaSO_4$ has very low aqueous phase solubility (2.4 mg/L at 20 °C, $K_{sp} = 1.1 \times 10^{-10}$).[25,26] During this precipitation process, the sulfate contribution to overall conductivity is replaced by conductivity contribution with two equivalent dissolved chloride ions. The equivalent conductivities (Λ) for 1/2 SO_4^{2-} and Cl^- are 80 and 76.3 cm^2 S/mol, respectively.[27] $BaSO_4$ precipitation results in a decrease in the overall conductivity due to the precipitation of SO_4^{2-} ions and dilution upon titration. For each removed SO_4^{2-} ion, two equivalents of Cl^- are added to the sample, mostly compensating for the conductivity deficit created by sulfate removal (−160.0 + 152.6 cm^2 S/mol). Therefore, the observed conductivity decrease is mainly the result of dilution. A more detailed mechanistic examination of the physical origins of individual conductivities, deviations in molar ionic conductivities for different species in different concentrations, and the accompanying Kohlrausch formalism is beyond the scope of this study.[28] After all of the sulfate has precipitated from solution, stepwise addition of $BaCl_2$ increases solution conductivity (Figure 2). By recording conductivity vs volume of the titrant added, one can readily observe when the slope of these data change from negative to positive. With this "endpoint", one can then quickly calculate the amount of sulfate in the original solution (Figure 2).

This technique's sensitivity limit was tested by titrating $MgSO_4$ solutions prepared in Millipore water (18.2 MΩ·cm resistivity). Our trials showed that, down to 100 mg/L, sulfate could be quantified with an accuracy of 7.6 mg/L. We note

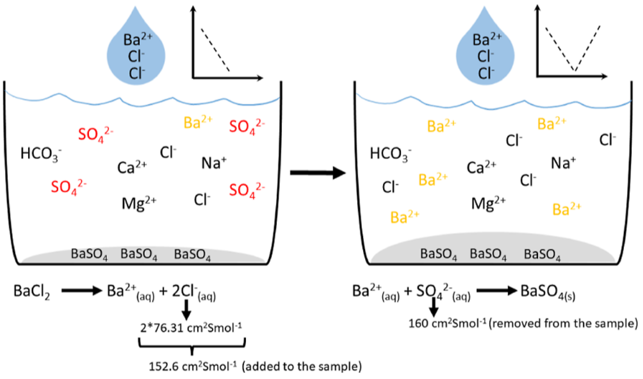


Figure 2. Scheme representing the principle of conductometric titration for sulfate analysis.

again that the EPA secondary contaminant level for sulfate is 250 mg/L,[13] demonstrating that this technique's accuracy is more than sufficient to assess water quality and its suitability for human and/or agricultural use.

Extending Method Generality (Cl^- Analysis). To test the ability of conductometric titration to quantify other inorganic ions in environmental aquatic systems, we also performed experiments to measure aqueous phase chloride concentrations. In this context, the chloride ion is commonly used as a natural tracer in ground and surface water systems.[29,30] Silver (Ag^+) was chosen as the complexation agent given AgCl's low solubility (1.6 mg/L at 20 °C).[25] Conductivity contributions from Cl^- ions in the sample are replaced by the conductivity of NO_3^- ions ($\Lambda\_ = 71.42$ cm² S/mol for NO_3^-), leading to a conductivity decrease.[27] After all the chloride has precipitated, further addition of $AgNO_3$ increases the overall conductivity of solution, and the amount of chloride can be calculated by using the end point in the titration curve.

Materials. Groundwater samples were collected from wells located in two watersheds on opposite sides of Rosebud Creek in southeast Montana. Surface water samples were acquired from Rosebud Creek itself, several miles upstream from Colstrip, MT (Figure 3). Samples were filtered through membranes with a 0.45 μm pore size and stored in closed containers until analyzed. Conductometric titrations for December 2020 and May 2021 samples were done with a PASCO wireless conductivity sensor (model PS-3210), while titrations for August 2021 samples and chloride analysis were done with a Mettler-Toledo FiveGo conductivity meter (model F3). Ion chromatography measurements for sulfate were performed using the EPA method 300.0 at the Montana Bureau of Mines and Geology (MBMG) Analytical Laboratory in Butte, Montana.[31] Details of this technique can be found in several sources including a standard operating procedure reported by the EPA,[32] as well as in the manual about best practices for quality assurance produced by the MBMG.[31] Solutions containing the complexation agent were prepared with Milli-Q ultrapure water having 18.2 MΩ·cm resistivity. $BaCl_2$ (anhydrous, Fisher Chemical) solutions used as a titrant for SO_4^{2-} precipitation were prepared with concentrations of 1800 mg/L.

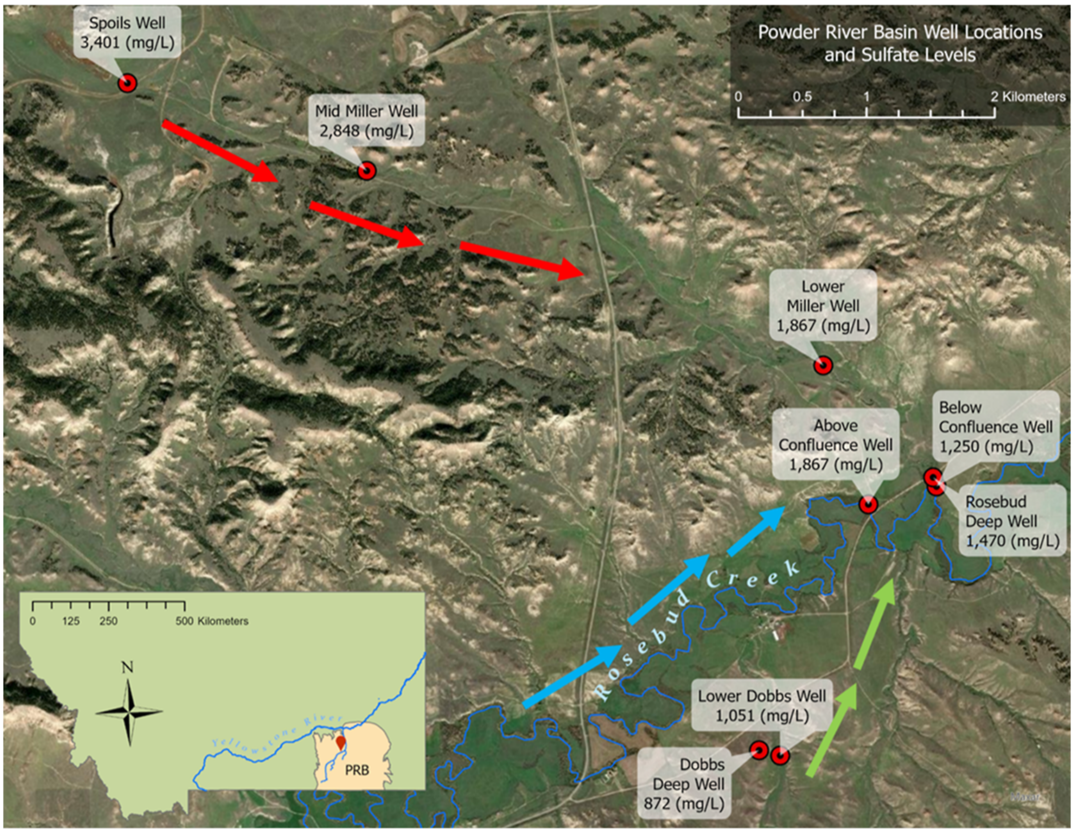


Figure 3. PRB map showing the locations where samples were collected from and sulfate levels in December 2020. The red arrows show groundwater flow from the reclaimed coal mine (Miller Coulee). The blue arrows show the surface water flow direction of Rosebud Creek. The green arrows show the groundwater flow from the undisturbed drainage (Dobbs Coulee).

Table 1. Concentrations of Selected Environmentally Related Ions (mg/L), pH, and Conductivities (μS/cm) from Samples Collected in December 2020 in Selected Sites[37]

	SO_4^{2-}	Cl^-	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	pH	conductivity
spoils well	3274	29.5	580.6	420.6	588.0	240.3	7.06	4606.8
below confluence well	1316	12.4	507.2	106.6	134.5	399.1	7.56	2884.8
RBC @ blw confluence	592.5	9.5	594.3	102.4	135.7	119.9	8.27	1808.0
Dobbs deep well	942.6	25.3	1186	153.6	225.6	250.0	7.14	2879.1

Table 2. Sulfate Concentrations in Ground (**Bold**) and Surface Water (*Italics*) from Sites Collected from and near Rosebud Creek (RBC) and a Comparison of Results Obtained from Both Conductometric Titration and IC[a]

sample location	titration SO_4^{2-} (mg/L)			IC—EPA method 300.0 data SO_4^{2-} (mg/L)[37]			percent difference		
	Dec-20	May-21	Aug-21	Dec-20	May-21	Aug-21	Dec-20	May-21	Aug-21
spoil well (36 ft)	3274	3450	3223.2	3401	3567	3299	−3.7	−3.3	−2.3
below confluence well (32 ft)	1316	1257	1252	1250	1169	1134	5.3	7.5	10.4
RBC @ blw conf	592.5	515.0	1142	553.2	470.4	1134	7.1	9.5	0.7
Dobbs deep well (104.5 ft)	942.6	898.6	866.5	872.1	818	852.2	8.1	9.9	1.7
RBC @ 39	570.6	456.1	1057	552	452.5	1034	3.4	0.8	2.2
RBC @ McRae	561.2	467.0	786.1	563.7	477.4	783.6	−0.4	−2.2	0.3
mid Miller well (17.7 ft)	2829	2446	2625	2848	2527	2545	−0.7	−3.2	3.1
Rosebud deep (93 ft)	1428	1390	1441	1470	1366	1444	−2.8	1.8	−0.2
lower Miller well (37.3 ft)	1804	1774	1819	1867	1829	1846	−3.4	−3.0	−1.4
lower Dobbs well (Dobbs shallow) (45 ft)	1038	947.5	916.7	1051	992.7	1034	−1.3	−4.5	−11.3
RBC @ Cow	640.3	521.1	1301	621.4	523	1294	3.0	−0.4	0.5
above confluence well (14.6 ft)	1678	2121	2261.6	1867	2119	2256	−10.1	0.1	0.2

[a]Numbers in parentheses in the first column indicate well depths.[37] Sampling site locations are reported in Figure 3 as well as in Table S1.

Chloride analyses were conducted for surface water samples collected from Bozeman Creek and three different locations on Upper Clark Fork River (UCFR). Chloride titration results are benchmarked against ion chromatography (IC) analysis in the Environmental Analytical Lab at Montana State University (EAL-MSU). IC measurements for chloride analysis used an AS18 column in Dionex ICS-2100 (Thermo Fisher Scientific, Inc.). Concentrations of $AgNO_3$ (99.5%, Fisher Chemical) used for chloride analyses varied between 430 and 720 mg/L.

■ RESULTS AND DISCUSSION

Environmental Samples (Sulfate Analysis). Researchers across Montana are engaged in a widespread effort to understand the impact of economic activity on water quality in local streams and rivers.[33−36] One result of this work has been the extensive cataloging of contaminants in several different watersheds.[37] Water samples tested for sulfate were taken from 8 different wells and 4 different surface water sites along Rosebud Creek in SE Montana. As noted in the introduction, this region is known for having high sulfate levels due to its geology. Open air coal mining results in even higher sulfate concentrations after land reclamation.[38] Locations of the sampling sites are shown in Figure 3, and precise geographic data and elevations are reported in the Supporting Information. Wells were installed in August 2020, and samples tested in this work were collected in December 2020, May 2021, and August 2021. Water temperatures were measured onsite, while pH and conductivities were measured not only onsite but also in the laboratory. Samples from each site were split for independent testing and analysis. These data are publicly available,[37] and concentrations of selected ions from the December 2020 measurements are reported in Table 1.

If sample conductivities were too high to be titrated with the stock $BaCl_2$ solution, samples were diluted with Millipore water (18.2 MΩ·cm resistivity). To check the accuracy of titration data, results were compared against independent measurements of total sulfur content using IC measurements according to EPA method 300.0. For the 36 different measurements, agreement between titration and IC data was quite good, with an averaged discrepancy of ±3.6% and a

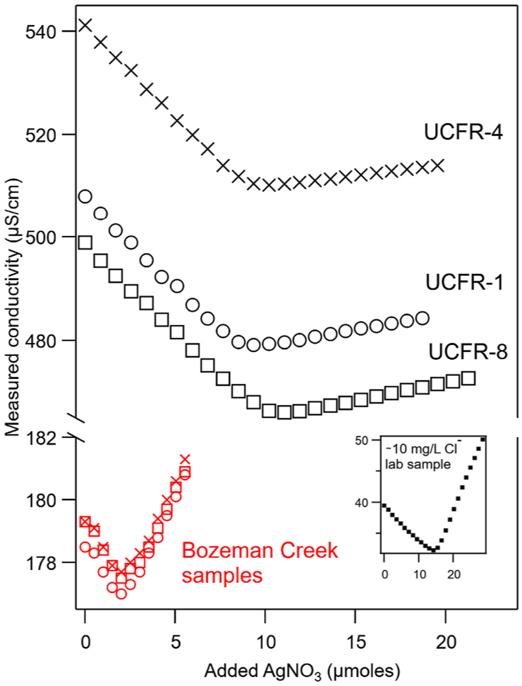


Figure 4. Chloride titration curves from a sample prepared with NaCl and Millipore water (bottom right) and environmental samples collected from Bozeman Creek (3 trials) and from three different locations on UCFR.

Table 3. Chloride Concentrations Determined by Conductometric Titrations and Ion Chromatography

	Cl^- concentration—conductometric titration (mg/L)	Cl^- concentration—Dionex ICS-2100 (mg/L)	percent difference (%)
Bozeman Creek (*n* = 3)	2.25 ± 0.1	1.92 ± 0.29	17.2
UCFR-1	10.21	10.04 ± 0.23	1.7
UCFR-4	10.81	10.26 ± 0.24	5.4
UCFR-8	11.99	11.84 ± 0.23	1.3

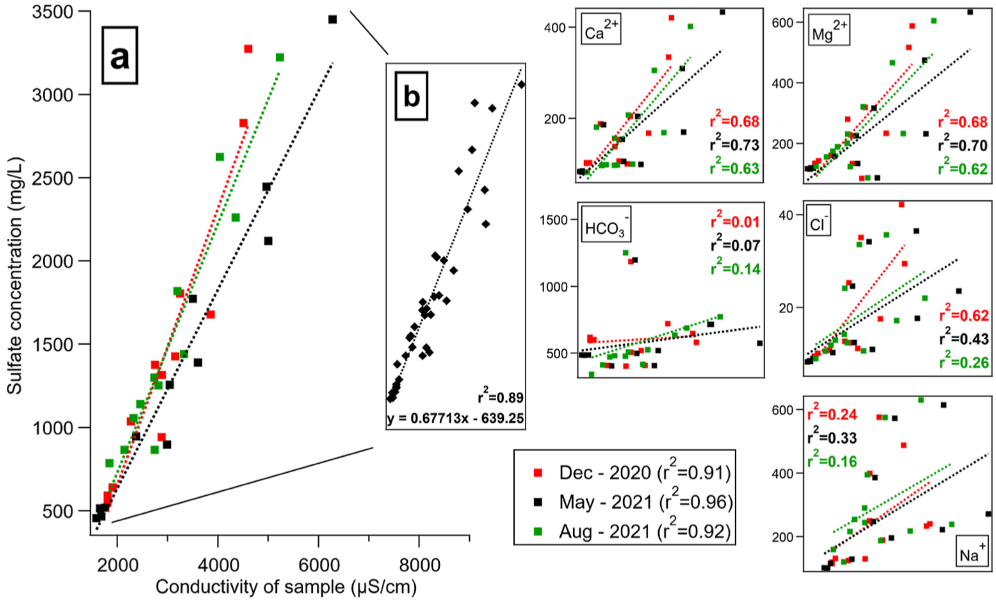


Figure 5. (a) Conductivity and individual ion concentration (SO_4^{2-}, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, and Na^+) correlations for three different sampling periods and (b) compiled correlation between conductivity and sulfate concentrations (three sampling periods combined). Concentrations on the *y*-axes are in mg/L.

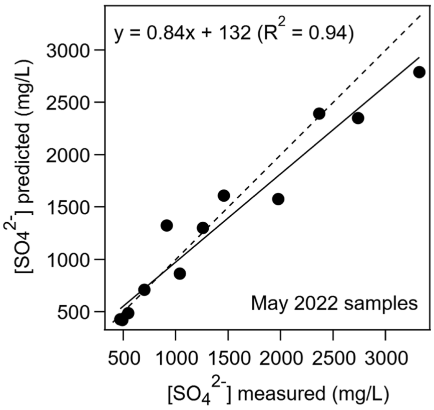


Figure 6. Correlation between predicted sulfate concentrations (*y* axis) and measured sulfate concentrations (*x* axis) using the correlation derived from sulfate–conductivity data shown in Figure 5b. The solid line shows the best linear fit to the data. The expression is included on the graph. The dashed line with a slope of 1.0 is included to illustrate ideal agreement.

maximum disagreement of 11.3%. Titration and IC data are summarized in Table 2. We note here that the time required to perform a titration (including preparing the $BaCl_2$ solution, setting up the titration assembly, and analysis) is approximately 2 h, and the "material cost" of an experiment is <$5, considering the conductivity meter and glassware as one-time-only capital equipment investments. Both metrics are attractive given the time and cost of sending field samples for analysis at an independent laboratory.

Environmental Samples (Chloride Analysis). Chloride analyses were performed using field samples taken from three separate sites along the Upper Clark Fork River and a local stream in Bozeman, MT. Independent testing of Cl^- concentrations was performed by the Montana State University Environmental Analytical Laboratory, also using ion chromatography. Conductometric titrations of these samples used $AgNO_3$ as the titrant to precipitate AgCl (Figure 4), and data comparing titration and ion chromatography results are reported in Table 3.

Like the samples tested for sulfate, the agreement between the titration and chromatography chloride measurements is quite good. Despite observing a large *percentage* difference between concentrations reported by the two methods for the lowest concentration samples (taken from Bozeman Creek), the *absolute* difference in Cl^- concentrations is 0.3 mg/L and falls within the uncertainties in ion chromatography results reported by the Montana State Environmental Analytical Lab. Additionally, for the UCFR samples having higher Cl^- concentrations, results between the two techniques agree to within 6%. Disagreement between measurements at low concentrations likely represents a limit to conductometric titration's ability to test for ion concentration. This limit will vary from species to species and depend on the complexation scheme used to precipitate the ion of interest out of solution.

Correlation between Conductivities and Sulfate Concentrations. The close agreement between sulfate concentrations in the groundwater and Rosebud Creek samples determined by conductometric titration and ion chromatography raises the question of whether an even simpler measurement can be used to determine ion concentrations in ground and surface water where the hydrogeology is well defined and historically cataloged. Figure 5a plots sulfate concentrations vs sample conductivity using sulfate concentrations measured by conductometric titration. Also shown in the smaller plots are the concentration data of five other ions vs conductivity. Data used for these figures are publicly available at the Ground Water Information Center (GWIC).[37] Ions were chosen based on their relative abundance. For individual data sets, the correlation between SO_4^{2-} concentrations and conductivity is high ($R^2 \geq 0.91$). Combining all of the sulfate concentrations across multiple data sets (Figure 5b) shows a slightly reduced correlation ($R^2 = 0.86$) but is still high enough to estimate sulfate concentrations based on conductivity measurements with reasonable confidence.

Not surprisingly, correlations between divalent cations Ca^{2+} and Mg^{2+} and bulk conductivities are observed—$R^2 = 0.68$ and 0.67, respectively—but not as strongly as for SO_4^{2-}. The correlation with monovalent anions and cations is very low. From these data, we propose that in the regions having high sulfate concentrations and where speciation data have been cataloged previously, a simple water conductivity measurement can be used to estimate sulfate concentrations. We tested this hypothesis using conductivity data from a new set of samples collected in May 2022. Using the correlation shown in Figure 5b, simple conductivity data predicted sulfate concentrations to within ±13%. A correlation between predicted and measured sulfate concentrations is shown in Figure 6. Conductivity and concentration data from the May 2022 samples are reported in the Supporting Information.

The agreement between predicted and measured sulfate concentrations is quite good ($R^2 = 0.94$) with deviations $\leq \pm 15\%$ in most cases. While the accuracy of sulfate concentrations predicted from conductivity would not be sufficient for careful quantitative analysis, we stress that results are more than accurate enough for local users of surface or groundwater to determine if sulfate concentrations are low enough so that water can be used for intended applications. Further work will be necessary before determining whether such close correlations hold for aqueous phase ions of interest in other environmental water samples.

■ CONCLUSIONS

The studies described above show conductometric titration to be capable of rapidly and accurately measuring sulfate concentrations in ground and surface water samples having high sulfate concentrations. Good agreement was observed between the titration-deduced sulfate concentrations and independent quantitative IC measurements by an EPA-approved method. The technique proved adaptable for also measuring ∼10 ppm chloride concentrations in different surface water samples. The chloride data agreed with independent IC analysis. Given the relative ease, speed, and accuracy of conductometric titration measurements, this technique stands out as an attractive means of assessing water quality quickly when end users must make real-time decisions with regards to water usage. Results presented in this study also indicate that low cost and publicly more accessible "conductivity-based" water analysis techniques can be developed in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.3c00126.

Detailed information of geographical information of sampling sites and sulfate concentrations in the samples collected from the same sites in May 2022 (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Galip Yiyen** formal analysis (lead), methodology (lead), writing-original draft (lead), writing-review & editing (equal); **Kodie V Duck** investigation (equal), methodology (equal); **Elizabeth Meredith** formal analysis (equal), project administration (equal), validation (equal), writing-review & editing (equal); **Robert A. Walker** funding acquisition (equal), project administration (equal), resources (equal), supervision (lead), writing-review & editing (lead).

Funding

This material is based upon the work supported in part by the National Science Foundation EPSCoR Cooperative Agreement OIA-1757351. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge Douglas and Kim McRae and the Greenleaf Land and Livestock Co. for allowing the authors to take field samples from wells on private land. The authors thank Dr. Toby Koffman from Montana State University's Environmental Analytical Laboratory for performing ion chromatography measurements on field samples to determine total chloride concentrations. The authors also thank Skye Keeshin for collecting field samples from the Upper

Clark Fork that were used for chloride analysis. The authors gratefully thank Andrew Hauer (University of Montana) for the original map used to create Figure 3, showing representative sulfate concentrations at different sampling sites along Rosebud Creek.

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