254

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Potentiometric Titration of Sulfate in Water and Soil Extracts Using a Lead-Mercury Amalgam Indicator Electrode[1]

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ABSTRACT

Sulfate concentrations in pure solutions, drainage waters, and soil saturation extracts were determined potentiometrically using a 70% Pb and 30% Hg amalgam indicator electrode and a saturated calomel reference electrode. Adjusting all samples to pH 4.7 allowed titration to a fixed potential on an automatic titrator. Sulfate concentrations ranging from 0.2 to 10 mmole/liter were determined by this method and compared with concentration determined by a turbidimetric method. Results from the two methods did not differ significantly, but the potentiometric titration method was more precise, sensitive, and rapid.

Additional Index Words: **automated titration.**

Current analytical procedures for SO_4^{2-} determinations in natural waters and saturated soil extracts are either time consuming or require specialized equipment not commonly available in the laboratory (3, 6, 7, 8, 9, 13). Because of analytical difficulties encountered, SO_4^{2-} concentrations are often obtained by the difference between the totals of measured anions and cations. A convenient analytical procedure is needed for routine SO_4^{2-} determinations to assure accurate data.

Potentiometric titrations of SO_4^{2-} with Pb^{2+} in water-organic solvent mixtures have recently been used to speed and simplify SO_4^{2-} determinations (2, 4, 9, 10). Cortellessa (2) used a lead-sensitive electrode prepared by immersing a Ag electrode in a $K_4Fe(CN)_6 \cdot 3H_2O$-$K_3Fe(CN)_6$ solution to measure SO_4^{2-} in solutions low in interfering ions. Ross and Frant (11) introduced a lead-sensitive Ag, Ag_2S, PbS electrode (10) that has been used to measure SO_4^{2-} in saturated soil extracts (4) and SO_4^{2-} oxidized from organic compounds (10). This electrode is subject to interferences from Cl^-, CO_3^{2-}-HCO_3^-, NO_3^-, PO_4^{3-}, Cu^+, Hg^+, and Ag^+ (5, 10, 11, 12). Many of these ions are present in natural waters and soil extracts.

The objectives of the research reported here were: (i) to construct a Pb-Hg amalgam indicator electrode that would react as an element in contact with a solution of its own ions, i.e. $Pb(s) = Pb^{2+} + 2e^-$; (ii) to determine its suitability as an analytical tool to measure SO_4^{2-} in natural waters and saturated soil extracts; and (iii) to adapt the electrode for use with an automatic titrator for rapid SO_4^{2-} determinations.

MATERIALS AND METHODS

Equipment and Reagents—The electrode was constructed by adding 12 g of Hg to 28 g of melted Pb in a 5-ml beaker that served as a mold. A 120- by 7-mm pyrex glass tube was placed partway into the molten metal, and one end of a multistrand Cu lead with the insulation removed from the last 20 mm was inserted down the glass tube and into the molten metal. A plexiglass cap was used on the electrode (Fig. 1). After the metal billet cooled, the glass mold was broken and removed, and the billet surface was smoothed on a small lathe. To avoid unnecessary human exposure to mercury vapor, the Pb was heated no more than required for melting, and the two metals were mixed under a fume hood.

Lead sulfate solubility in aqueous solution is 1.4×10^{-4} *M* at 25C (14), which is too high for potentiometric titration. Several solvents have proved effective in lowering the $PbSO_4$ solubility when added to aqueous solution (2, 5, 11, 12). Methanol, ethanol, and isopropanol were compared and found to be suitable for use with the automatic titration procedure. A 1:1 isopropanol/water mixture was selected for subsequent work. All samples, standards, and titrants were prepared with this solvent/water ratio in order to shorten mixing and reaction time between sample and titrant.

During the preliminary work the titrant was dispensed with a 2.0-ml micrometer buret into the samples as they were mixed with a magnetic stirrer. The voltage was measured with the indicator electrode described above and a saturated calomel reference electrode on a pH meter. The endpoint was determined as the inflection point of the titration curve. During the preliminary work it became evident that the endpoint potential was pH dependent. Titration to a fixed potential was possible only if the samples and standards were adjusted to the same pH before adding the solvent. This permitted the latter part of this work to be carried out on an automatic titrator.

Ionic Strength, Specific Ion, and pH Effects—The ionic

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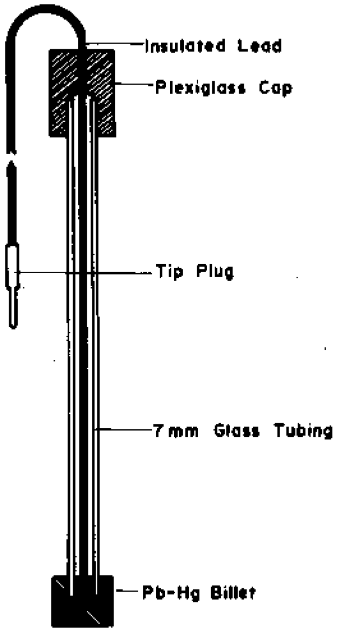

Fig. 1—Lead-mercury amalgam indicator electrode.

strength, specific ion, and pH effects on the SO_4^{2-} titration curves were measured by titrating Na_2SO_4 in isopropanol-water mixtures containing the factor to be studied. Sodium perchlorate was used to determine the ionic strength effects of dissolved salts. Isopropanol-water mixtures containing 0.2, 0.4, 1.0, 2.0, 4.0, or 10.0 mmole/liter Na_2SO_4 and 0, 2.5, and 25 times as much $NaClO_4$ as Na_2SO_4 on a molar basis were prepared. These were manually titrated with 50 mmole/liter $Pb(ClO_4)_2$ as described above.

Chloride and NO_3^- effects were determined in the same manner using the Na^+ salts and compared to ClO_4^- ion to distinguish between ionic strength and specific ion effects. Phosphate interference at 0.02 and 1.3 mmole/liter $H_2PO_4^-$ were determined. Carbonate and HCO_3^- interferences were removed by automatically titrating all samples to pH 4.7.

Sulfate is not titrated stoichiometrically by $Pb(ClO_4)_2$ solution (12). This may be caused by complex-ion formation, double-salt precipitation, or formation of mixed precipitates. As the SO_4^{2-} concentration in samples increases, disproportionally less $Pb(ClO_4)_2$ is required to reach the inflection point on the titration curve, but the inflection voltage is unchanged. In the work reported here, standards bracketing the unknowns were used and an "effective strength" for the titrant was determined for each unknown from a standard curve.

To determine the precision of the method and to compare it with a turbidimetric method (13), SO_4^{2-} was determined eight times on water samples from each of three subsurface drains by both methods. Duplicate SO_4^{2-} determinations were also made by both methods on soil saturation extracts from six horizons of an unclassified Aridisol and from the surface 10 cm of six agricultural soils.

RESULTS AND DISCUSSION

Ionic Strength, Specific Ion, and pH Effects—Ionic-strength increases resulting from $NaClO_4$ additions decreased sharpness of the titration curve at the inflection point (Fig. 2). The loss of sharpness was manifest at all SO_4^{2-} concentrations, but does not pose a serious problem in titration.

Nitrate in solution at five times the SO_4^{2-} concentration exhibited the same effect as did ClO_4^{2-} at the same concentration. At 50 times the SO_4^{2-} concentration, NO_3^- caused a slight decrease in the voltage after the inflection point was reached. This effect would not be serious in the rare cases where NO_3^- may be extremely high. The same pattern was observed at all SO_4^{2-} concentrations tested. This indicated that NO_3^- could replace ClO_4^- in the procedure.

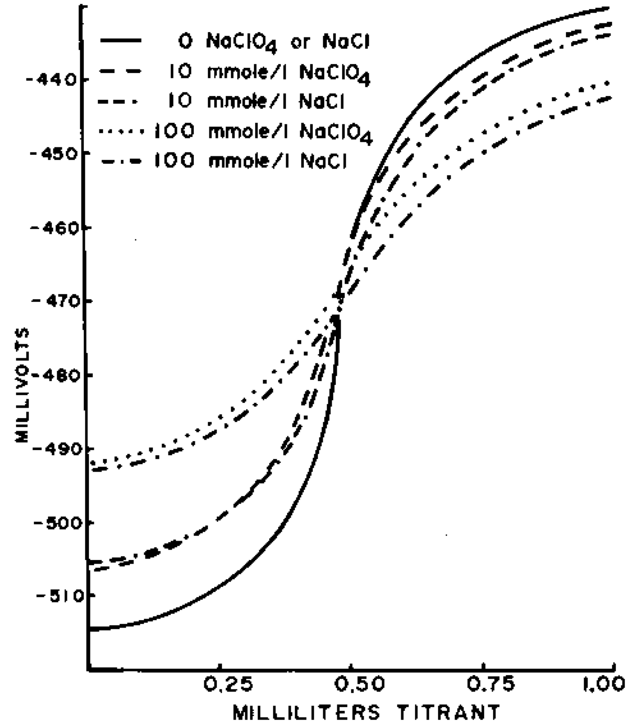

Fig. 2—Titration of 0.025 mmole Na_2SO_4 with 50 mmole/liter $Pb(ClO_4)_2$ as effected by $NaClO_4$ or NaCl.

At all concentrations tested, Cl^- interfered by shifting the titration curve to a slightly lower voltage (Fig. 2). The shift is easily compensated for by adding Cl^- to the standards in approximately the same concentration as in the unknowns (10).

Phosphate, as indicated (5), did not interfere at concentrations below 0.02 mmole/liter, but 1.3 mmole/liter PO_4^{3-} in 2 mmole/liter SO_4^{2-} interfered by forming insoluble $PbHPO_4$. Phosphate concentrations in natural waters and soil extracts rarely exceed 0.02 mmole/liter and thus are not expected to interfere.

Preliminary work showed that the endpoint potential was pH dependent (Fig. 3) and that titration to a fixed potential was possible if the pH of all standards and samples were held constant. This permitted development of a procedure that could be used with an automatic titrator. The use of automatic titrators have not been reported with the potentiometric titration procedures cited (2, 5, 11, 12). Carbonate and HCO_3^- interfere with Pb^{2+} titration of SO_4^{2-} since $PbCO_3$ is less soluble than $PbSO_4$. As the pH increases more $PbCO_3$ forms, and below pH 3.0 $Pb(HSO_4)_2$ forms. Since pH 4.7 is the equivalent point for HCO_3^- titration with strong acid, all samples and standards were adjusted to pH 4.7 before the SO_4^{2-} was determined.

Figure 4 shows the titration curve for a subsurface drain-

Table 1—Results from eight sulfate determinations by two methods on three subsurface drainage waters

		SO_4^{2-}	Standard deviation	Coefficient of variation
		mmole/liter		%
Sample site:	Method			
Fish hatchery:	Turbidimetric	1.04	0.11	5.47
	Potentiometric	1.01	0.02	1.15
Hankins:	Turbidimetric	1.65	0.27	8.21
	Potentiometric	1.69	0.05	1.55
Tolbert:	Turbidimetric	2.25	0.15	3.42
	Potentiometric	1.60	0.17	4.06

age water and a saturated soil extract. The samples were adjusted to pH 4.7 with $HClO_4$, diluted with an equal volume of isopropanol and manually titrated.

Precision of Method—Sulfate in samples from three subsurface drainage waters was determined turbidimetrically (11) and potentiometrically. The means of eight replications obtained by the two methods did not differ significantly. The standard deviations and coefficients of variation were generally smaller for the potentiometric titration method (Table 1). Duplicate SO_4^{2-} determinations on saturated soil extracts from six horizons of a noncultivated Aridisol (Natrargid) and samples from six cultivated soils were determined by both methods. Results from the two procedures did not differ significantly (Table 2).

When compared with a turbidimetric method, the results of the titration procedure were not significantly different, but were generally more precise. Using a quick-change syringe, 30 to 50 CO_3^{2-} and HCO_3^- or 25 to 30 SO_4^{2-} determinations per hour were made using an automatic titrator by the procedure described.

These results show that the easily constructed Pb-Hg amalgam electrode can be adapted for the automatic titration of SO_4^{2-} in natural waters and saturated soil extracts. The electrode is easily cared for. Precipitate removal from the billet with a paper towel after each day of use was the only maintenance required. Failure to keep the electrode surface clean could possibly result in the formation of a SO_4^{2-} sensitive Pb(Hg), $PbSO_4$(s) electrode (4); however, this was not encountered during this study. The electrode responded well at concentrations from 0.2 to 10 mmole/liter SO_4^{2-}.

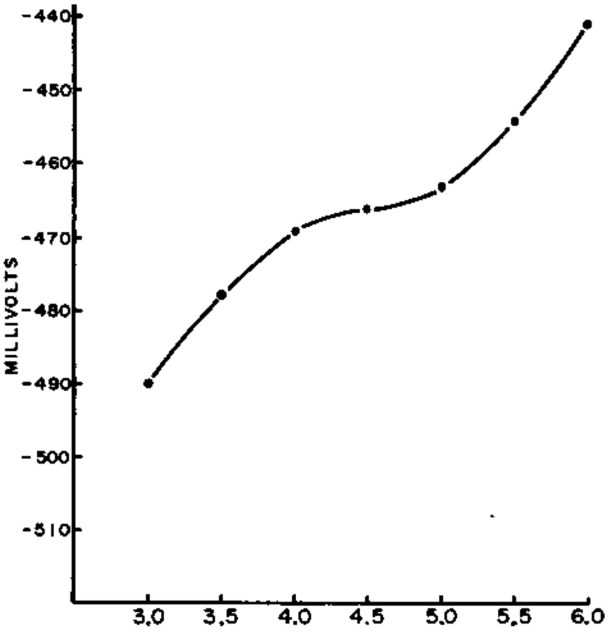

Fig. 3—Inflection point voltage as effected by pH adjustment of sample containing 200 mmole/liter $NaHCO_3$ and 1 mmole/liter Na_2SO_4.

Table 2—Sulfate analysis by potentiometric titration and turbidimetric methods on saturated extracts from six horizons of a noncultivated Aridsol (Natrargid) and six cultivated soils

		SO_4^{2-} determined	
		Potentiometric	Turbidimetric
Noncultivated aridisol		mmole/liter	
Depth cm	Horizon		
0 - 1	A-2	0.88	0.75
1 - 13	B-21	11.55	10.75
13 - 35	B-22_{sa}	45.46	44.56
35 - 45	C-1_{casa}	39.00	39.88
45 - 50	C-2_{casa}	38.23	37.38
50 - 60	C_{cam}	32.25	32.13
Cultivated soils (surface 10 cm)			
Portneuf		1.63	1.43
Minidoka		5.45	5.80
Purdam		0.26	0.19
Sciam		3.59	3.73
Greenleaf		1.16	1.00
Nyssaton		1.95	1.92

Recommended Procedure— Aliquots containing between 0.008 and 0.4 mmole/[redacted] SO_4^{2-} are diluted to 40 ml with water and titrated to pH 4.7 with $HClO_4$. If CO_3^{2-} and HCO_3^- are of interest, they can be measured at this point by using standardized acid on an automatic titrator. The samples are then diluted to 50 ml with water, and 50 ml of isopropanol are added.

The samples are then titrated to —465 mV with a 1:1 isopropanol/water mixture containing 10 mmole/liter Pb-

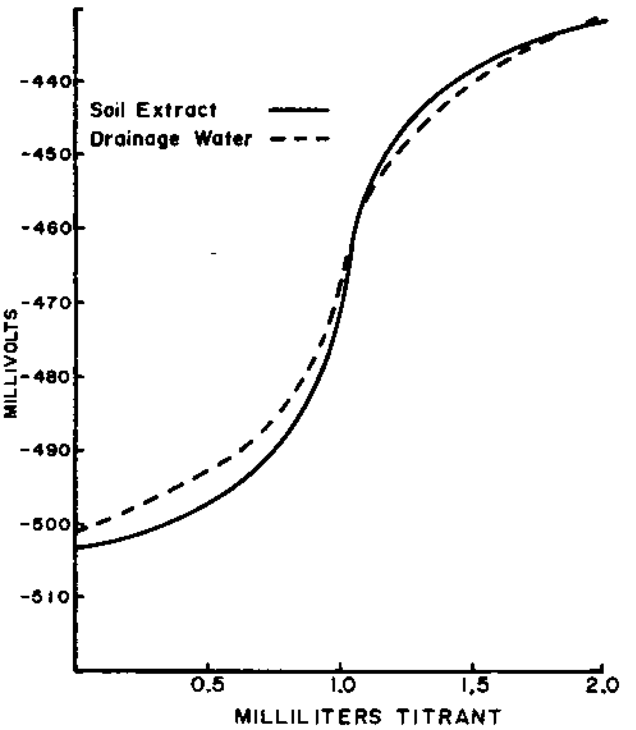

Fig. 4—Ten-ml aliquot of saturated soil extract from Minidoka silt loam diluted to 25-ml and a 25-ml aliquot from Tolbert drainage tunnel, each titrated with 50 mmole/liter $Pb(ClO_4)_2$.

$(ClO_4)_2$ that has been standardized against 1:1 isopropanol/water mixtures with SO_4^{2-} concentrations bracketing the SO_4^{2-} concentrations in the unknowns. The Fisher Automatic Titralyzer with a quick-change syringe assembly or similar apparatus works very well for these titrations (Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the products listed by the U.S. Department of Agriculture).

The titrant delivery tip is placed within 1 mm of the indicator electrode billet in order for the titralyzer to anticipate the endpoint. The titralyzer print delay control is set at 45 sec because of the slow reaction rate in samples with low SO_4^{2-} concentrations. The delay control is used to set the length of time between the last titrant addition and the printing of the titrant volume before proceeding to the next sample.

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