AMERICAN
Environmental
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10/92

Suspended organic matter removal from aqueous extracts of high pH soils

By Charles W. Robbins

In order to pursue the sodic soil reclamation research, it was necessary to develop a pretreatment method for sodic soil extracts that would simultaneously remove the HCO_3^- ion and suspended organic matter interferences without adding additional interferences.

Organic matter and clay minerals in soils have negatively charged surfaces that act much like cation exchange resins. When more than 15% of the exchange sites are neutralized by Na^+ and the final ionic strength of the aqueous extract is less than about 0.04 *M*, the clays and organic matter are dispersed. Under these conditions, the solution pH is usually greater than 8.4, and carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) are present in the extracts. The dispersed organic matter stays in suspension (up to 0.2% by weight) and causes the extracts to be dark colored.[1] These unusually high-pH, high-sodium soils are designated as sodic or sodic soils. Ion chromatography (IC) has been adapted for anion analysis in soil extracts by Nieto and Frankenberger and by Skarie et al.[2,3] The soils used in those studies had pH values below 8.2. Consequently, the soil extracts probably did not contain the dispersed organic matter usually associated with high-sodium soil extracts.

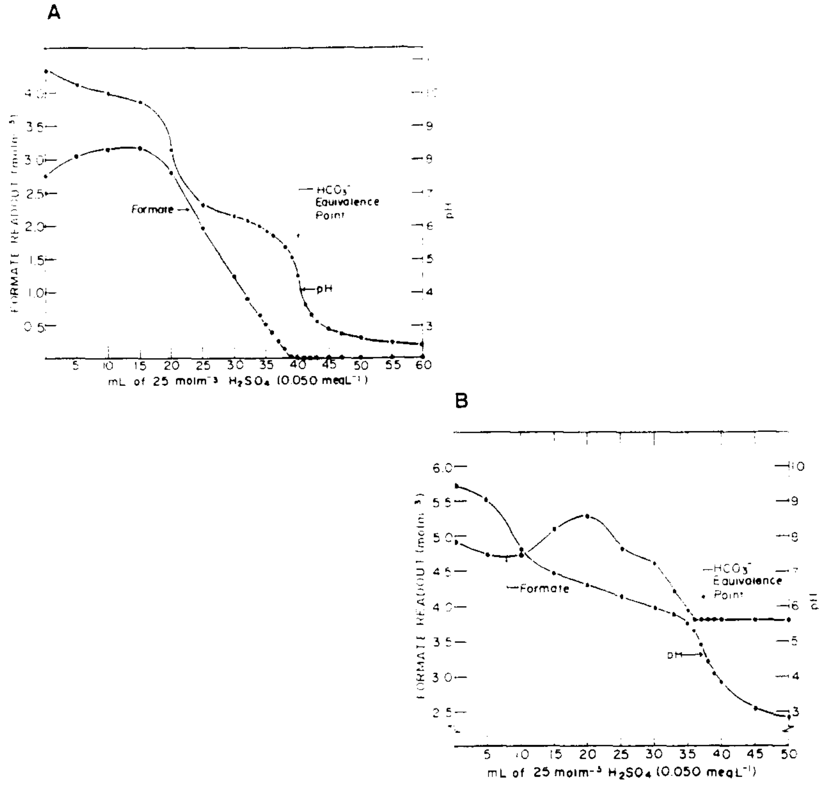

Figure 1a *and* **b** *Formate results and pH of solutions containing CO_3^{2-} and HCO_3 as affected incremental additions of H_2SO_4 to samples that contained no formate and extracts that contained 3.8 mM formate.*

A study of cropping and amendment effects on sodic soil reclamation rates and mechanisms required analysis of a large number of dark-colored, high-organic-matter extracts.[4] Formate and acetate were produced in the soil as a result of some of the treatments. These two ions may be an important factor in reclaiming sodic soils, even though they have not previously been analyzed. While analyzing the high pH extracts for formate ion by IC, it was found that formate and HCO_3^- ions elute at the same time. Suspended organic matter in the extracts plugged and, in some cases, permanently damaged the IC exchange columns, even though the extracts had been filtered through 0.2-µm nylon filters. Commercially available filters designed to remove

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suspended matter became plugged before sufficient sample was collected for IC analysis, or allowed excessive organic matter through the filters, which in turn plugged the IC columns.

In order to pursue the sodic soil reclamation research, it was necessary to develop a pretreatment method for sodic soil extracts that would simultaneously remove the HCO_3^- ion and suspended organic matter interferences without adding additional interferences. An additional IC requirement is that the final samples have a low total ionic strength.[5] An ideal pretreatment procedure would provide clear samples that could be analyzed by the new IC methods as well as the traditional methods in use by many laboratories.

Materials and methods

The samples used to test this cleanup method were selected from aqueous extracts collected during a sodic soil reclamation study.[4] The samples were selected such that all exchangeable sodium percentages were greater than 15. The sodic soil extract pH values were between 8.5 and 10.1, and the extract ionic strengths were less than 0.04 *M*. The combination of high pH and low ionic strength in these extracts produced high concentrations of suspended organic matter in the extracts. Additionally, saline-sodic soil extracts that have pH values less than 8.2 and ionic strengths greater than 0.04 *M* were selected for comparison with the sodic soil extracts. The saline-sodic extracts were clear, and free from suspended organic matter because of the lower pH and higher ionic strengths than in the sodic soil extracts. All extracts discussed in this paper were prepared by the standard procedures used for preparing saturation paste extracts.[6]

The suspended organic matter content in the extracts was measured by adjusting the extracts to pH 3.0 to 3.5 with 1.0 *M* HCl, followed by making the solution 2.5 m*M* Al^{3+} with 50 m*M* $AlCl_3$.[7] The extracts were then centrifuged for 5 min at 4000 rpm and passed through oven-dried (60 °C overnight) preweighed filter papers. Each filter paper, plus organic matter, was then oven dried, reweighed, and the suspended organic matter content determined.

Two solution series were made up to verify the steps required to remove the HCO_3^- interference in the IC formate analyses. The first series consisted of 21 100-mL aliquots of 10 m*M* Na_2CO_3. To each was added a different volume of 25 m*M* H_2SO_4 over the range 0 to 60 mL (*Figure 1a*). The solutions were made up to a final volume of 200 mL. The second series consisted of 16 50-mL aliquots of a sodic soil extract (pH 9.4) that contained 3.8 m*M* formate, 4.1 m*M* CO_3^{2-}, and 29.3 m*M* HCO_3^-. Different volumes of 25 m*M* H_2SO_4 over the range 0 to 50 mL (Figure 1*b*) were added to the extracts, and they were then made up to 100 mL. The CO_2 produced by the reactions between the H_2SO_4 and the CO_3^{2-} and HCO_3^- was removed by placing the samples and extracts in an ultrasonic water bath at room temperature while applying a vacuum to the containers. The pH and formate concentrations were measured and the results were plotted (Figures 1*a* and *b*).

Once it was determined that the organic matter could be easily removed from the dark extracts, that the HCO_3^- interference could be removed, and that HCO_3^- and CO_3^{2-} analyses could be performed in the same process, sets of clear and dark extracts were selected to determine if this method could be used to prepare sodic and saline-sodic soil extracts for IC analysis. The clear extracts were from saline-sodic soils and contained very little organic matter. The sodic soil extracts contained 10 to 2000 mg/L^{-1} dark red to black organic material that could be removed by acidification, Al^{3+} addition, centrifugation, and filtration. The dark extracts selected were too dark to be analyzed by colorimetric or turbidimetric methods and contained sufficient suspended organic matter to plug the IC columns. All extracts were titrated with standardized 1.0 *M* HCl or 0.5 *M* H_2SO_4 to determine CO_3^{2-} (pH 8.4) and HCO_3^- (pH 4.7) using a 2.0-mL microburet, a pH meter, and combination electrode.[8] The extracts were further acidified to pH 3.0 to 3.5.

Twelve clear soil extracts that were 0 to 6 m*M* acetate and 0 to 4 m*M* formate and titrated to a pH of 3.0 to 3.5 with H_2SO_4 were each divided into two equal portions. Half of each extract was treated with $Al_2(SO_4)_3$, as described earlier, while the other was not. Acetate and formate concentrations were determined by injecting a 20-µL sample into a 2-m*M* potassium benzoate eluant stream (pH 6.0) pumped through a Waters IC-PAC™ anion exchange column (Waters Chromatography Div., Millipore Corp., Milford, Massachusetts) at 1.5 mL/min^{-1}.

A Waters model 430 five-electrode flow-through IC conductivity detector was used to measure the ion concentrations. The results were plotted and calculated by a Waters 740 data module integrating recorder. Under these conditions, acetate and formate eluted at about 3.3 and 4.0 min, respectively. Results from the extracts receiving Al^{3+} were compared with those receiving no Al^{3+} (*Table 1*).

The 12 extracts from the acetate-formate IC analyses, plus six additional clear extracts with higher Cl^- concentrations that had also been adjusted to pH 3.0 to 3.5, were divided in half, and one-half of each extract was treated with $Al_2(SO_4)_3$. Those 24 subsamples were analyzed for Cl^- by IC using the same procedures as used for the acetate and formate analysis. Chloride elutes at about 5.6 min by that method. Those extracts were also analyzed for Cl^- by Ag^+ titration.[6] An additional 18 dark sodic extracts were pH adjusted, Al^{3+} added, centrifuged, and the supernatant liquid was filtered through a 0.2-µm filter. These extracts were analyzed by IC and Ag^+ titration. When present, NO_2^- and NO_3^- elute at about 7.6 and 10.1 min under these IC conditions.

Ten clear extracts containing 2 to 44 m*M* SO_4^{2-} and ten dark extracts containing 2 to 12 m*M* SO_4^{2-} were titrated to pH 3.0 to 3.5 with 1 *M* HCl. Each clear extract was divided into equal portions. One-half was analyzed turbidimetrically[9] and $AlCl_3$ was added to the other, followed by IC analysis. The dark extracts were treated with 1.0

Table 1 **Comparison of various methods for analyzing anions in high pH soil extracts**

Anions	Method X	Pretreat. X	Method Y	Pretreat. Y	No. samples	Conc. range (m*M*)	Regression*	Corr. coeff. (*r*)
Acetate (clear)	IC	None	IC	$Al_2(SO_4)_3$	12	0-6	Y=-0.067+1.005X	0.991
Formate (clear)	IC	None	IC	$Al_2(SO_4)_3$	12	0-4	Y=0.072+0.998X	0.992
Cl (clear)	Ag	None	Ag	$Al_2(SO_4)_3$	18	1-130	Y=0.042+0.979X	0.989
Cl (clear)	Ag	$Al_2(SO_4)_3$	IC	$Al_2(SO_4)_3$	18	1-130	Y=0.121+1.033X	0.986
Cl (dark)	Ag	$Al_2(SO_4)_3$	IC	$Al_2(SO_4)_3$	18	1-8	Y=0.130+1.017X	0.988
SO_4 (clear)	Turbid.	None	Turbid.	$AlCl_3$	10	2-44	Y=-0.371 + 0.992X	0.989
SO_4 (clear)	Turbid.	$AlCl_3$	IC	$AlCl_3$	10	2-44	Y=-0.373 + 1.007X	0.983
SO_4 (dark)	Turbid.	$AlCl_3$	IC	$AlCl_3$	10	2-12	Y=-0.107 + 1.003X	0.990

*X represents the results of the more conventional method or treatment and Y represents the new method or the new treatment.

mL 0.08 m*M* $AlCl_3$, centrifuged, and filtered through 0.2-μm filters. These extracts were analyzed turbidimetrically and by IC. The IC eluant for SO_4^{2-} analysis was 1.0 m*M* potassium phthalate (pH 6.5), pumped at 1.5 mL/min^{-1} through the IC-PAC anion exchange column. Chloride, NO_2^-, NO_3^-, and SO_4^{2-} elute at about 2.5, 3.2, 4.6, and 6.9 min, respectively, under these conditions. The Cl^- added in the pretreatment often caused the Cl^- and NO_2^- peaks to overlap.

No comparisons were made between Al^{3+} treated and untreated dark extracts by any of the anion analysis methods because of the interferences mentioned.

Results and discussion

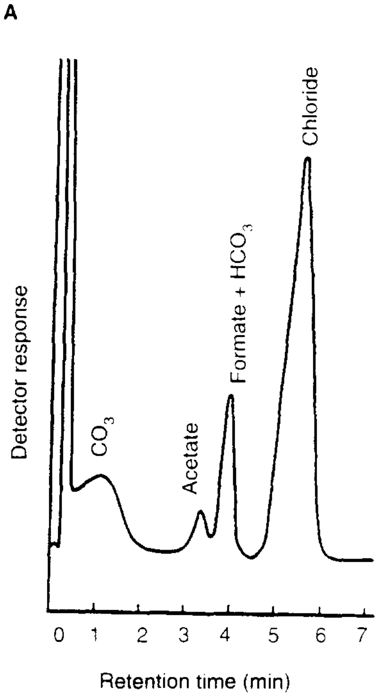
Formate analysis by IC in the presence of HCO_3^- resulted in an overestimation of formate. To verify the nature of this overestimation, two sets of solutions were made up. The first contained 10 m*M* $NaCO_3^-$, and the second, a sodic soil extract, contained 4.1 m*M* CO_3^{2-}, 29.3 m*M* HCO_3^-, and 3.8 m*M* formate. Varying amounts of 25 m*M* H_2SO_4 were added to each solution sample and the pH and formate concentrations were measured and plotted (Figures 1*a* and *b*). In both cases, the pH decreased as acid was added, with a sharp pH drop, as the last CO_3^{2-} was converted to HCO_3^- (pH 8.4), and again as the last HCO_3^- was converted to H_2CO_3 (pH 4.7). The formate results in the first case (Figure 1*a*) responded to HCO_3^- concentration, first slightly increasing as the pH decreased and the CO_3^{2-} was converted to HCO_3^-, and then, as the HCO_3^- was converted to H_2CO_3 and CO_2, the formate results decreased rapidly to zero just prior to the solution pH having reached the H_2SO_4—HCO_3^- titration equivalence endpoint at pH 4.7. Figure 1*a* shows that the HCO_3^- must be removed prior to formate analysis. A similar but less ideal set of curves is produced with the titration and formate analysis of the sodic soil extract (Figure 1*b*). Once the pH is below about 5.0, the formate results remain constant with decreasing pH.

Figure 2a shows an IC trace of a sodic soil extract prior to acidification, and Figure 2*b* shows the same extract after adjusting the pH to 3.3. Lowering the pH and converting the CO_3^{2-} and HCO_3^- to H_2CO_3 and CO_2 removed the CO_3^{2-} peak and decreased the area of the formate-HCO_3^- peak to that of formate only, without affecting the acetate or Cl^- results.

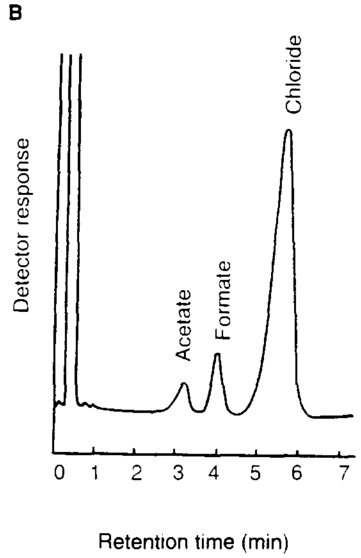
Organic matter coagulation from aqueous solution, particularly public water supplies, include shocking the system by changing the pH (raising or lowering), followed by adding a cation source, usually an aluminum salt, and then filtering the coagulated material. The most effective procedure in each case is determined by the original pH and the particular organic materials being removed.[7] The sodic soil extracts selected to test this pretreatment method contained from 20 to 2100 mg/L^{-1} of suspended organic matter. They were too dark for colorimetric and turbidimetric analysis, even when diluted, and they contained sufficient suspended materials to plug the IC exchange columns.

It was determined that for these extracts, if the pH were adjusted to 3.5 or below, and the solution made about 2.5 m*M* Al^{3+} with $AlCl_3$ or $Al_2(SO_4)_3$, the suspended material flocculated and nearly all of the color was removed from solution. The flocculated material could be centrifuged and filtered from solution. Above pH 3.5, the Al^{3+} was not consistently effective, and below 3.0, the IC conductivity detector did not recover from the water peak in time to detect acetate. It was also found that the pH had to be adjusted before the Al^{3+} addition; otherwise a much higher Al^{3+} concentration was required to flocculate the organic matter.

Linear regression analysis was made comparing pH-adjusted, Al^{3+}-pretreated clear extracts with pH-adjusted, clear extracts with no Al^{3+} added and analyzed for acetate and formate by IC (Table 1, lines 1 and 2). The regression slopes were very nearly 1.0; the absolute intercept values for Y were less than 0.08 m*M*, and the correlation coefficients were greater than 0.99.



Column: Waters IC-PAC anion column: detector: conductivity: eluant: 2.0 m*M* benzoate: flow rate: 1.5 mL/min^{-1}: sample volume: 20 uL: sample: sodic soil extract: pH=3.3: CO_2: 4.8 m*M*: HCO_3: 4.3 m*M*; acetate: 2.1 m*M*; formate: 3.8 m*M*; Cl : 6.1 m*M*.



Column: Waters IC-PAC anion column: detector: conductivity: eluant: 2.0 m*M* benzoate: flow rate: 1.5 mL/min^{-1}: sample volume: 20 µL: sample: sodic soil extract adj. to pH=3.3: CO_3: 0.0 m*M*: HCO_3: 0.0 m*M*: acetate: 2.1 m*M*: formate: 3.8 m*M*: Cl: 6.1 m*M*.

Figure 2a *and* **b** *Saturation paste extract IC chromatograms before and after CO_3^{2-} and HCO_3^- interference removal by lowering the pH and the dissolved CO_2 concentrations.*

These data show that the Al^{3+} had no effect on the organic anion IC results under these conditions. Methyl orange was organically used as a pH indicator to titrate the extracts to 4.7 for the HCO_3^- analysis,[6] but its use was discontinued because it plugged the IC columns.

Three comparisons are shown for Cl^- analysis (Table 1, lines 3, 4, and 5). The first comparison was between clear pH-adjusted extracts, with and without $Al_2(SO_4)_3$ addition, analyzed by Ag^- titration using chromate as the endpoint indicator.[6] The second comparison was between Ag^+ titration and IC analysis of pH-adjusted, clear extracts treated with $Al_2(SO_4)_3$. The third comparison was between Ag^- titration and IC analysis of dark extracts that had been clarified by pH adjustment, Al^{3+} addition, centrifugation, and filtration. The regression values for the Cl^- data were not quite as ideal as the previous data, but still showed that the pretreatment did not produce a significant difference in the results. The two analytical procedures were also not significantly different. No attempt was made to compare analysis of Cl^- in the dark extracts by either procedure without first removing the organic matter.

Three comparisons were made for SO_4^{2-} analysis (Table 1, lines 6, 7, and 8). The first comparison was between clear, pH-adjusted extracts, with and without $AlCl_3$ addition, by the turbidimetric method.[9] The second comparison was between turbidimetric and IC analysis of clear extracts that had been pH adjusted and $AlCl_3$ added. The third comparison was between turbidimetric and IC analysis of dark extracts that had been pH adjusted, Al^{3+} added, centrifuged, and filtered. The regression analysis shows that the Al^{3+} addition did not affect the results, nor was there a difference between the two procedures (Table 1, lines 6, 7, and 8). Data were not compared between treated and untreated dark extracts.

Conclusions

Colloidal organic matter can be removed from sodic soil saturation paste extracts by acidifying the extracts, to pH 3.0 to 3.5, adding Al^{3+}, centrifuging the extract, and then filtering it through a 0.2-µm nylon filter. By using standardized acid, CO_3^{2-} and HCO_3^- concentration can be determined during the cleanup process by titrating to pH 8.4 and then to 4.7, and the HCO_3^- interference removed for formate analysis by IC. Once the extracts are clarified, they can be analyzed for Cl^- and SO_4^{2-} by traditional and IC methods used for saline and sodic soil extracts as well as acetate, formate, NO_3^-, and NO_2^- by IC methods without further sample preparation. When used as a pH indicator, methyl orange plugged the anion column, thus precluding colorimetric pH titration and removal of HCO_3^-.

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