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 HCO₃⁻ 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 (CO₃²⁻) and bicarbonate (HCO₃⁻) 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.

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. 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.

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. 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 HCO₃⁻ 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...
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 mM Al$_{3+}$ with 50 mM 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 mM Na$_2$CO$_3$. To each was added a different volume of 25 mM H$_2$SO$_4$ 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 mM formate, 4.1 mM CO$_2^-$ and 29.3 mM HCO$_3^-$. Different volumes of 25 mM H$_2$SO$_4$ over the range 0 to 50 mL (Figure 1b) were added to the extracts, and they were then made up to 100 mL. The CO$_2$ produced by the reactions between the H$_2$SO$_4$ and the CO$_2^-$ and HCO$_3^-$ was removed by placing the samples and extracts in an ultrasonic water bath at room temperature while allowing a vacuum to the containers. The pH and formate concentrations were measured and the results were plotted (Figures 1a 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$_2^-$ 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$^4$ 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$_2$SO$_4$ to determine CO$_2$ (pH 8.4) and HCO$_3^-$ (pH 4.7) using a 2.0-mL microburet, a pH meter, and combination electrode.$^5$ The extracts were further acidified to pH 3.0 to 3.5.

Twelve clear soil extracts that were 0 to 6 mM acetate and 0 to 4 mM formate and titrated to a pH of 3.0 to 3.5 with H$_2$SO$_4$ were each divided into two equal portions. Half of each extract was treated with Al$_{3+}$(SO$_4$)$_2$, as described earlier, while the other was not. Acetate and formate concentrations were determined by injecting a 20-μL sample into a 2-mL potassium benzoate eluant stream (pH 6.0) pumped through a Waters IC-PAC(TM) 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$_{3+}$(SO$_4$)$_2$. 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.$^0$ 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 mM SO$_4^{2-}$ and ten dark extracts containing 2 to 12 mM 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$^7$ and AlCl$_3$ was added to the other, followed by IC analysis. The dark extracts were treated with 1.0
Comparison of various methods for analyzing anions in high pH soil extracts

<table>
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<th>Anions</th>
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<th>Method Y</th>
<th>Pretreat. Y</th>
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*X represents the results of the more conventional method or treatment and Y represents the new method or the new treatment.

Results and discussion

Formate analysis by IC in the presence of HCO₃⁻ resulted in an overestimation of formate. To verify the nature of this overestimation, two sets of solutions were made up. The first contained 10 mM Na₂CO₃, and the second, a sodic soil extract, contained 4.1 mM CO₃²⁻, 29.3 mM HCO₃⁻, and 3.8 mM formate. Varying amounts of 25 mM H₂SO₄ were added to each solution sample and the pH and formate concentrations were measured and plotted (Figures 2a and b). In both cases, the pH decreased as acid was added, with a sharp pH drop, as the last CO₃⁻ was converted to HCO₃⁻ (pH 8.4), and again as the last HCO₃⁻ was converted to H₂CO₃ (pH 4.7). The formate results in the first case (Figure 2a) responded to HCO₃⁻ concentration, first slightly increasing as the pH decreased and the CO₃⁻ was converted to HCO₃⁻, and then, as the HCO₃⁻ was converted to H₂CO₃. In the formate results, the formate results decreased rapidly to zero just prior to the solution pH reaching the H₂CO₃—HCO₃⁻ titration equivalence endpoint at pH 4.7. Figure 2a shows that the HCO₃⁻ 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 2b). 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 2b shows the same extract after adjusting the pH to 3.3. Lowering the pH and converting the CO₃⁻ to HCO₃⁻ to H₂CO₃, and CO₂ removed the CO₂⁻ peak and decreased the area of the formate (HCO₃⁻) 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. 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 mM Al³⁺ with AlCl₃, or Al₂(SO₄)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 Al³⁺ 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 Al³⁺ addition; otherwise a much higher Al³⁺ concentration was required to flocculate the organic matter.

Linear regression analysis was made comparing pH-adjusted, Al³⁺-pretreated clear extracts with pH-adjusted, clear extracts with no Al³⁺ added and analyzed for acetate and formate by IC (Table 1, lines 1 and 2). The regression slopes were very near 1.0; the absolute intercept values for Y were less than 0.08 mM, and the correlation coefficients were greater than 0.99.
These data show that the Al\textsuperscript{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\textsubscript{3}\textsuperscript{-} analysis, but its use was discontinued because it plugged the IC columns.

Three comparisons are shown for Cl\textsuperscript{-} analysis (Table 1, lines 3, 4, and 5). The first comparison was between clear pH-adjusted extracts, with and without Al\textsubscript{3}(SO\textsubscript{4})\textsubscript{3} addition, analyzed by Ag\textsuperscript{+} titration using chromate as the endpoint indicator. The second comparison was between Ag\textsuperscript{+} titration and IC analysis of pH-adjusted, clear extracts treated with Al\textsubscript{3}(SO\textsubscript{4})\textsubscript{3}. The third comparison was between Ag\textsuperscript{+} titration and IC analysis of dark extracts that had been clarified by pH adjustment. Al\textsuperscript{3+} addition, centrifugation, and filtration. The regression values for the Cl\textsuperscript{-} 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\textsuperscript{-} in the dark extracts by either procedure without first removing the organic matter.

Three comparisons were made for SO\textsubscript{4}\textsuperscript{2-} analysis (Table 1, lines 6, 7, and 8). The first comparison was between clear, pH-adjusted extracts, with and without AlCl\textsubscript{3} addition, by the turbidimetric method. The second comparison was between turbidimetric and IC analysis of clear extracts that had been pH adjusted and AlCl\textsubscript{3} added. The third comparison was between turbidimetric and IC analysis of dark extracts that had been pH adjusted, Al\textsuperscript{3+} added, centrifuged, and filtered. The regression analysis shows that the Al\textsuperscript{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\textsuperscript{3+}, centrifuging the extract, and then filtering it through a 0.2-μm nylon filter. By using standardized acid, CO\textsubscript{3}\textsuperscript{2-} and HCO\textsubscript{3}\textsuperscript{-} concentrations can be determined during the cleanup process by titrating to pH 8.4 and then to 4.7, and the HCO\textsubscript{3}\textsuperscript{-} interference removed for formate analysis by IC. Once the extracts are clarified, they can be analyzed for CO\textsubscript{3}\textsuperscript{2-} by traditional and IC methods used for saline and sodic soil extracts as well as acetate, formate, NO\textsubscript{3}\textsuperscript{-}, and NO\textsubscript{2} \textsuperscript{-} 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\textsubscript{3}\textsuperscript{-}.

References


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