Sample Preparation for Determining Ions in Dark Colored Sodic Soil Extracts

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ABSTRACT

Saturation paste extracts of sodic soils (pH >8.5 and electrical conductivity <4.0 dS m^{-1}) usually contain dark colored, suspended organic matter that interferes with colorimetric, turbidimetric, potentiometric, ion chromatographic (IC) and to a lesser extent, atomic absorption spectrophotometry and flame emission procedures. Bicarbonate also interferes with formate analysis by IC in those extracts. This study was conducted to develop a simple pretreatment method for removing those interferences without introducing new interferences. Fifteen mL extract samples were titrated to pH 8.4, then to 4.7 and finally to a pH range of 3.0 to 3.5 with standardized H$_2$SO$_4$ or HCl. The first two end points determine CO$_3^{2-}$ and HCO$_3^-$ concentrations. The third pH adjustment removed the HCO$_3^-$ interference from the formate analysis and allowed for organic matter coagulation. The acid choice depended on whether Cl$^-$ or SO$_4^{2-}$ was to be measured later. To remove the organic matter, the extracts were centrifuged and forced through a 0.2-μm nylon filter following 0.08 M AlCl$_3$ or 0.04 M Al$_2$(SO$_4$)$_3$ treatments. Formate and acetate concentrations were determined by IC. The Cl$^-$ concentrations were determined by colorimetric, and IC procedures. The SO$_4^{2-}$ concentrations were measured turbidimetrically and by IC. The extracts were analyzed for Ca^{2+} and Mg^{2+} by atomic adsorption spectrophotometry, and Na$^+$ and K$^+$ by flame emission. Titrating the extracts as described provided CO$_3^{2-}$ and HCO$_3^-$ data, removed the HCO$_3^-$ interference from the formate analysis, and allowed Al^{3+} to coagulate the suspended organic matter, which was then removed by centrifugation and filtration. This pretreatment did not interfere with any of the analytical methods tested, except for cation determination by IC and anion determination by IC when methyl orange was used as a pH end point indicator.

S ODIC SOILS and natric horizons are designated as having exchangeable sodium percentages (ESP) in excess of 15 and/or sodium adsorption ratios (SAR) in excess of 13 (mM L^{-1})$^{1/2}$ and electrical conductivities (EC) of <4.0 dS m^{-1} in the saturation paste extracts (Soil Survey Staff, 1975). The saturation paste pH in sodic soils is, by definition >8.4 (U.S. Salinity Laboratory Staff, 1954). The high pH and low ionic

strength in sodic soils disperses many soil organic materials. The old term "black alkali" came from the observation that these materials moved to the soil surface with evaporating water and covered the soil particles with a black oily looking coating.

Titration methods using color change end points such as carbonate (CO$_3^{2-}$) and bicarbonate (HCO$_3^-$), pH titrations, or chloride (Cl$^-$) titration with silver (Ag$^+$) in the presence of chromate cannot be seen in the dark extracts. Turbidimetric sulfate (SO$_4^{2-}$) analyses are also inaccurate when the suspended material is present. The suspended organic matter in the extracts frequently caramelize in flame emission and atomic absorption spectrophotometer burner heads and gradually change the sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) calibration curves.

Ion chromatography (IC) has recently been adapted for cation (Basta and Tabatabai, 1985; Nieto and Frankenberger, 1985b) and anion (Nieto and Frankenberger, 1985a; Skarie et al., 1987) analysis in soil extracts. The soils used in those studies had pH values below 8.4. Consequently, the soil extracts probably did not contain the dispersed organic matter usually associated with sodic 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 was produced in the soil by some of the treatments (Robbins, 1986). These two ions may be an important factor in reclaiming sodic soils, even though they have not previously been measured. Suspended organic matter in those extracts plugged, and in some cases, permanently damaged the IC exchange columns, even though the extracts had been filtered through 0.2-μm filters. Another problem encountered when analyzing the high pH extracts for formate ion, was that formate and HCO$_3^-$ ions elute at the same time when determined by IC.

The purpose of this project was to develop a pretreatment method for sodic soil extracts that would simultaneously remove the HCO$_3^-$ ion, dark color and suspended organic matter interferences without adding additional interferences. An additional IC requirement is that the final samples have a low total ionic

strength (Basta and Tabatabai, 1985). An ideal pretreatment procedure would provide 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 soil samples used in this study were selected from samples collected during a reclamation study (Robbins, 1986). All samples were from saline-sodic or sodic phases of a Declo sandy loam (coarse-loamy, mixed, mesic, Xerollic Calciorthids). The cation exchange capacities ranged from 220 to 260 mM charge kg^{-1} (Robbins, 1984). The samples were selected such that all ESPs were greater than 15 and all SARs were greater than 13 (mM L^{-1})$^{1/2}$. The sodic soil saturation paste pH values were between 8.5 and 10.1, and the saturation paste extract ECs were less than 4.0 dS m^{-1}. The combination of high pH and low EC in these soils produced dark colored extracts due to the high concentrations of suspended organic matter in the extracts. The saline-sodic saturation paste pH values were less than 8.3 and the extract ECs were greater than 4.0 dS m^{-1}. These extracts were clear, and free from suspended organic matter because of the lower

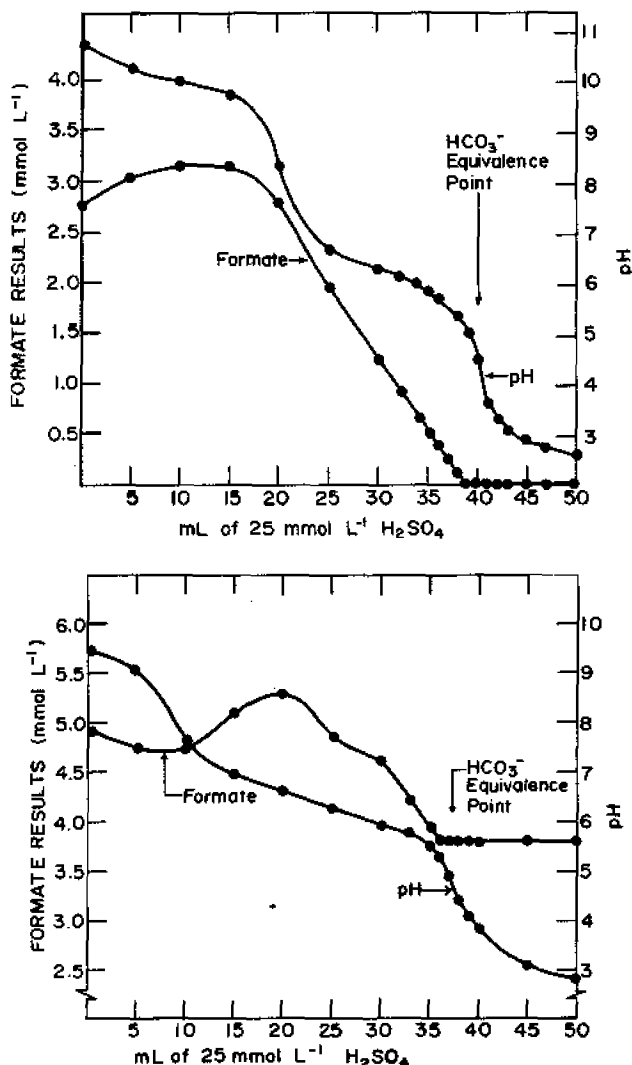Fig. 1a,b. Formate results and pH of solutions containing CO_3^{2-} and HCO_3^- as affected by incremental additions of H_2SO_4 to samples that contained no formate and extracts that contained 3.8 mM L^{-1} formate.

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 (U.S. Salinity Laboratory Staff, 1954).

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 M AlCl$_3$ (Dempsey et al., 1984). The extracts were then centrifuged for 5 min at 4000 rpm and passed through ovendried (60 °C overnight), preweighed filter papers. Each filter paper, plus organic matter, was then oven-dried, reweighed, and the suspended organic matter content was calculated.

Two series of solutions were made up to determine 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 (Fig. 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 L^{-1} formactions between the H$_2$SO$_4$ and the CO$_3^{2-}$ and HCO$_3^-$ was volumes of 25 mM H$_2$SO$_4$ over the range 0 to 50 mL (Fig. 1b) were added to the extracts and then they were made up to 100 mL. The majority of the CO$_2$ produced by the reactions between the H$_2$SO$_4$ 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 (Fig. 1a,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 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 extracts for the various analytical methods used for saline, sodic, and saline-sodic soil extracts. The clear extracts (no color in extract) were from saline-sodic soil samples 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, centrifuging, and then 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$_3^{2-}$ (pH 8.4) and HCO$_3^-$ (pH 4.7) using a 2.0 mL microburette, and pH meter and a combination electrode (Stumm and Morgan, 1970). 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$_2$(SO$_4$)$_2$ as described earlier while the other half was not. Acetate and formate concentrations were determined by injecting a 20-μL sample in to a 2 mM potassium benzoate eluent stream (pH 6.0) being pumped through a Waters IC-PAC (Waters Chromatography Division, Millipore Corp., Milford, MA)[1] anion exchange column 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}.

The 24 subsamples from the acetate-formate IC analyses

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[1] Names of equipment manufacturers and suppliers are provided for the benefit of the reader and do not imply endorsement by the Dep. of Agriculture.

plus six additional clear extracts with higher Cl⁻ concentrations that had also been adjusted to pH 3.0 to 3.5, divided in half, and one-half of each treated with $Al_2(SO_4)_3$, were analyzed for Cl⁻, using the same IC procedures, used for the acetate and formate analysis. Chloride elutes at about 5.6 min by that method. Those extracts were also analysed for Cl⁻ by Ag⁺ titration (U.S. Salinity Laboratory Staff, 1954). 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 also analyzed for Cl⁻ 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 L⁻¹ SO_4^{2-} and 10 dark extracts containing 2 to 12 mM L⁻¹ SO_4^{2-} were titrated to pH 3.0 to 3.5 with 1 M HCl. The clear extracts were divided into equal portions and $AlCl_3$ was added to half of each extract. Both portions were analysed turbidimetrically (Tabatabai and Bremner, 1970) and the $AlCl_3$ treated portions were analysed by IC. The dark extracts were treated with 1.0 mL of 0.08 mM $AlCl_3$, centrifuged, and filtered through 0.2-μm filters. These extracts were analyzed turbidimetrically and then by IC. The IC eluent used for SO_4^{2-} analysis was 1.0 mM 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.

Sixteen clear and sixteen dark extracts were selected to give a wide range of Ca^{2+}, MG^{2+}, Na^+, and K^+ concentration ranges. Each extract was analysed for Ca^{2+} and Mg^{2+} by atomic absorption spectrophotometry (AA) and for K^+ and Na^+ by flame emission (FE). The clear extracts were also analysed for the four cations by IC. Each extract was then divided into two equal portions and the pH was adjusted to 3.0 to 3.5, one half with 1.0 M HCl and the other with 0.5 M H_2SO_4. The $AlCl_3$ was added to the first half, and $Al_2(SO_4)_3$ was added to the second half. The extracts were centrifuged, filtered, and the cations again measured on the same samples. The Ca^{2+} and Mg^{2+} IC eluent was 0.5 mM ethylenediamine (pH 6.0) and the K^+ and Na^+ eluent was 2.0 mM HNO_3. The flow rate in both cases was 1.2 mL min⁻¹. Separate Waters IC-PAC cation columns were used for the divalent and monovalent ions. Under those conditions Mg^{2+} and Ca^{2+} eluted at 3.4 and 5.4 min and Na^+, and K^+ eluted at 2.0 and 3.2 min respectively.

RESULTS AND DISCUSSION

Formate analysis by IC in the presence of HCO_3^- resulted in an overestimation of formate concentration. To verify the nature of this overestimation, two sets of solutions were made up, the first was 10 mM $NaCO_3^-$, and the second a sodic soil extract, contained 4.1 mM L⁻¹ CO_3^{2-}, 29.3 mM L⁻¹ HCO_3^- and 3.8 mM L⁻¹ formate. Varying volumes of 25 mM H_2SO_4 were added to each solution sample and the pH and formate concentrations were measured and the results plotted (Fig. 1a,b). In both cases, the pH decreased as acid was added, with a sharp 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 H_2SO_4-HCO_3^- titration endpoint or equivalence point shown in the figures being that point at which essentially all CO_3^{2-} and HCO_3^- was converted to H_2CO_3 and aqueous

CO_2 (Stumm and Morgan, 1970). The formate results in the first case (Fig. 1a) responded to HCO_3^- concentration, first slightly increasing as the pH decreased
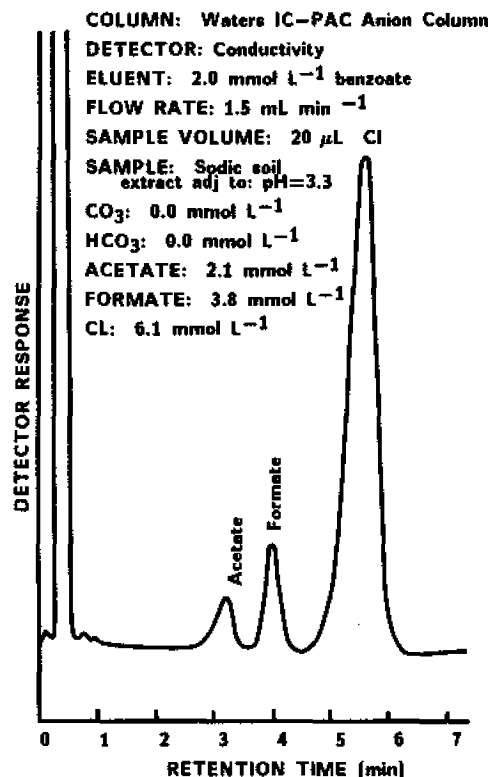

COLUMN: Waters IC–PAC Anion Column
DETECTOR: Conductivity
ELUENT: 2.0 mmol L⁻¹ benzoate
FLOW RATE: 1.5 mL min⁻¹
SAMPLE VOLUME: 20 μL
SAMPLE: Sodic soil extract: pH=3.3
CO_3: 4.8 mmol L⁻¹
HCO_3: 4.3 mmol L⁻¹
ACETATE: 2.1 mmol L⁻¹
FORMATE: 3.8 mmol L⁻¹
Cl: 6.1 mmol L⁻¹

COLUMN: Waters IC–PAC Anion Column
DETECTOR: Conductivity
ELUENT: 2.0 mmol L⁻¹ benzoate
FLOW RATE: 1.5 mL min⁻¹
SAMPLE VOLUME: 20 μL Cl
SAMPLE: Sodic soil extract adj to: pH=3.3
CO_3: 0.0 mmol L⁻¹
HCO_3: 0.0 mmol L⁻¹
ACETATE: 2.1 mmol L⁻¹
FORMATE: 3.8 mmol L⁻¹
CL: 6.1 mmol L⁻¹
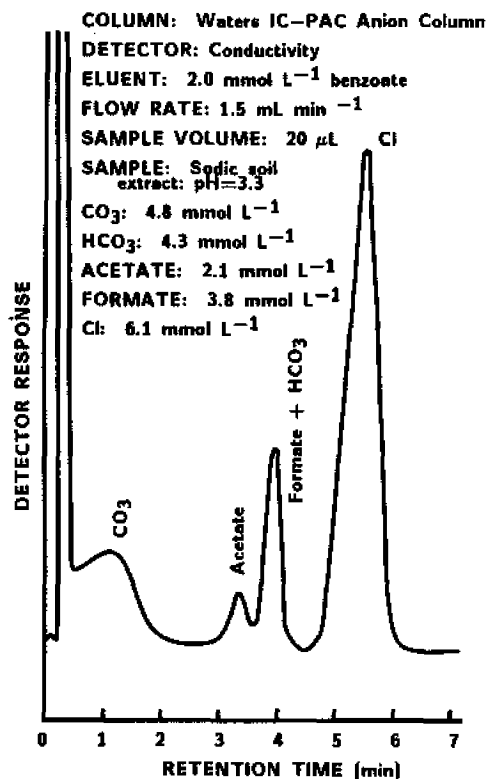
Fig. 2a,b. Saturation paste extract IC chromatograms before and after CO_3^{2-} and HCO_3^- interference removal by lowering the pH and HCO_3^- concentration.

and as 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. This figure shows that the HCO_3^- must be removed prior to formate analysis. A similar but less ideal set of curves was produced with the titration and formate analysis of the sodic soil extract (Fig. 1b). Once the pH was 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 Fig. 2b shows the same extract after the pH was adjusted to 3.3. Lowering the pH and converting most of 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 effecting the acetate and Cl^- results.

Organic matter coagulation from aqueous solution, particularly public water supplies methods, include shocking the system by changing the pH (raising or lowering) followed by addition of a cation source, usually an Al salt, and then filtering the coagulated material. The most effective procedure in each case was determined by the original pH and the particular organic materials being removed (Dempsey et al., 1984). 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 was adjusted to 3.5 or below and the solution made about 2.5 mM 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 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+} addi-

tion, otherwise a much higher Al^{3+} concentration was required to flocculate the organic matter.

Linear regression analysis was made comparing Al^{3+}, pH-adjusted, 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 mM, and the correlation coefficients were greater than 0.99. 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 (U.S. Salinity Laboratory Staff, 1954), but its use was discontinued because it also 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 (U.S. Salinity Laboratory Staff, 1954). 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. No attempt was made to analyze for Cl$^-$ by potentiometric titration, since it was assumed that the organic matter would consume at least some Ag$^+$ from solution as the Cl$^-$ concentration decreased during the titration, thereby overestimating the Cl$^-$ concentration.

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 (Taba-

Table 1. Comparison of various methods for analyzing anions and cations in sodic and saline-sodic soil extracts.

	Method X	Pre-treatment X	Method Y	Pre-treatment Y	No. of samples	Concentration range	Regression†	Correlation coefficient
						mM L^{-1}		
				Anions				
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$_4^{2-}$ (Clear)	Turbid.	None	Turbid.	AlCl$_3$	10	2–44	$Y = -0.371 + 0.992X$	0.989
SO$_4^{2-}$ (Clear)	Turbid.	AlCl$_3$	IC	AlCl$_3$	10	2–44	$Y = -0.373 + 1.007X$	0.983
SO$_4^{2-}$ (Dark)	Turbid.	AlCl$_3$	IC	AlCl$_3$	10	2–12	$Y = -0.107 + 1.003X$	0.990
				Cations				
Ca^{2+} (Clear)	AA	None	AA	Al Salts	16	4–50	$Y = 0.037 + 0.997X$	0.994
Ca^{2+} (Dark)	AA	None	AA	Al Salts	16	1–3	$Y = -0.013 + 1.006X$	0.996
Mg^{2+} (Clear)	AA	None	AA	Al Salts	16	4–30	$Y = -0.031 + 0.998X$	0.996
Mg^{2+} (Dark)	AA	None	AA	Al Salts	16	1–4	$Y = 0.005 + 0.999X$	0.996
Na$^+$ (Clear)	FE	None	FE	Al Salts	16	1–105	$Y = -0.058 + 1.011X$	0.998
Na$^+$ (Dark)	FE	None	FE	Al Salts	16	8–52	$Y = 0.013 + 1.004X$	0.997
K$^+$ (Clear)	FE	None	FE	Al Salts	16	1–12	$Y = 0.002 + 0.997X$	0.998
K$^+$ (Dark)	FE	None	FE	Al Salts	16	2–11	$Y = 0.004 + 1.003X$	0.998

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

tabai and Bremner, 1970). 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 show 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.

Initially, it appeared that the cations could be analyzed in the Al^{3+} treated solutions by IC, but the cation columns were gradually saturated with Al^{3+} and the mono- and divalent cations were no longer fully retained. Flushing the columns with 6 M HNO_3 or KOH did not rejuvenate the columns. They appeared to be permanently poisoned. When atomic adsorption spectrophotometry analysis for Ca^{2+} and Mg^{2+} and flame emission analysis for Na^+ and K^+ were made on extracts with and without the addition of either Al^{3+} salt and the results were evaluated by regression analysis. No differences in the results were shown to be caused by the Al^{3+}. These tests were made on both clear and dark extracts (Table 1, lines 9 through 16).

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