MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

COMMUNICATIONS IN SOIL SCIENCE AND PLANT ANALYSIS
Vol. 33, Nos. 15–18, pp. 3377–3388, 2002

POSTER PAPER

COPING WITH EFFECTS OF HIGH DISSOLVED SALT SAMPLES ON THE INDUCTIVELY COUPLED PLASMA SPECTROMETER

Jane E. Hislop* **and James W. Hornbeck**

USDA Forest Service, Northeastern Research Station, 271
Mast Road, P.O. Box 640, Durham, NH 03824

ABSTRACT

Research on acidic forest soils typically uses unbuffered salt solutions as extractants for exchangeable cations. Our lab uses 1 M NH_4Cl extractant for exchangeable cations (Ca, K, Mg, and Na) and 1 M KCl for exchangeable aluminum. The resulting high dissolved salt solutions presented chronic analytical problems on flame atomic absorption spectrophotometer (AAS) and direct current plasma spectrometer (DCP). More recently, the analyses completed on a simultaneous, axial inductively coupled plasma-atomic emission spectrometer (ICP-AES) have continued to be problematic. Although ICP manufacturers provide application notes that list some precautions to help minimize the salt effect, such issues are seldom mentioned in published articles and can be misleading when interpreting results. This paper describes various

---

*Corresponding author. Fax: (603) 868-7604; E-mail: jhislop@fs.fed.us

DOI: 10.1081/CSS-120014531
0010-3624 (Print); 1532-2416 (Online)
www.dekker.com

modifications that have been tried to eliminate the effects of high dissolved salts when using ICP. Adjustable parameters such as gas flow rates, sample introduction rates, dilution rates, and accessories were tested. Results of each modification were evaluated by comparing method detection limits, recovery rates, and carry-over values to determine the most effective operating ICP system. For example, a 15 second increase of sample uptake and rinse times for the KCl method decreased the method detection limit (MDL) by 12%, recovery rate by 12%, and carry-over by 25%.

INTRODUCTION

Extractants made from unbuffered salts are the accepted methods for determining exchangeable cations in acidic forest soils. Exchangeable cations (Ca, K, Mg, and Na,) are analyzed from 1 M NH_4Cl extractant and exchangeable aluminum is measured from 1 M KCl extractant.[1] Although these extractants have been used for decades, it is seldom mentioned in published articles that they present chronic analytical problems.

Several methods papers have pointed out the problems when analyzing high salt samples. The *Quality Assurance Methods Manual for Laboratory Analytical Techniques* stated, "Aspiration of 1 N NH_4Cl will probably clog most burner assemblies on emission and atomic spectrometers."[1] Amacher et al.[2] offered a combined extractant that the salt concentrations were "not so high that they will create problems for the ICPES torch." In the 1990 EPA *Handbook of Methods for Acid Deposition Studies,* "The most common physical interference in the analysis of soils exchange solutions is salt build-up clogging the burner or nebulizer." was reported by Blume et al.[3] *Determination of Metals in Brines by ICP-AES*[4] specified, "The analysis of metals in brine solutions presents many difficult problems. Two of the primary concerns are problems with ionization from the alkali and alkaline earth metals, and the problem of clogging of nebulizer and injector tubes when using high concentrations of salts in solution." Again, Johnson[5] wrote "when analyzing samples with high salt contents, there is always the potential problem of plugging sample introduction components." In *Determination of Exchangeable Acidity and Exchangeable Aluminum in Soils* Coscione[6] mentioned, "however, the use of KCl solutions has been questioned, considering its clogging effect on nebulizers and its corrosion effects on the spectrometers used to determine the cations."

These articles provided several modifications to minimize the salt effect. "Dilution with ammonium acetate is recommended as a matrix modifier to reduce or eliminate problems from clogging of aspirators during analysis" was offered in

Quality Assurance Methods Manual for Laboratory Analytical Techniques.[1] Amacher et al.[2] proposed using a combined $NH_4Cl-BaCl_2$ extractant with salt concentrations sufficient to obtain exchangeable cations without creating problems with the torch. The EPA Methods Handbook considered "dilution will reduce this problem, it will also change the matrix and any effect it may have on the instrument read-out."[3] In the *Determination of Metals in Brines by ICP-AES*[4] suggested "brine analysis often requires longer rinse times applied at a higher frequency and dilution of the sample may be required for major constituent determination." Johnson[5] stated, "Analyzing high salt solutions may require the addition of an argon saturator accessory to the instrument and longer rinse times between samples." Coscione et al.[6] proposed using NH_4Cl or NH_4NO_3 as alternative soil extractants.

The suggestions from ICP-AES manufacturers to alleviate these analytical problems can be found in their operation manuals and application notes. Common advice includes using an argon saturator, increasing the auxiliary flow rate, lowering the injector tube, and on an axial instrument, increasing both the plasma and auxiliary gas flows.

An excellent source of hints is from other analysts. Examples of their operation modifications include using specific spray chambers and nebulizers, using wide bore injector (2.3 ml or wider), diluting the samples 5 to 10 times due to the "salting out" in the axial torch, reducing sample uptake with smaller pump tube (0.4 ml/min), using another extractant such as ammonium acetate and using various dilution solutions such as weak acid (HCl and HNO_3) and triton-X.

In the work we report here, the analytical problems have been addressed by adjusting parameters such as gas flow rates, sample introduction rates, dilution rates, and accessories modifications. The determination of the optimum operational conditions for high dissolved salt samples became the objective of this process.

MATERIALS AND METHODS

To test the effects of these adjustments we evaluated recovery rates (RR), method detection limits (MDL), and carry-over values (COD) (Figs. 1 and 2; Tables 1 and 2). This manuscript presents the comparison of the aluminum analyses for NH_4Cl and KCl extractions only to illustrate the adjustment changes from the three hardware setups and ten parameter modifications. The three ICP-AES hardware setups are: 1) twister spray chamber and seaspray nebulizer (TSS), 2) struman-master spray chamber and v-groove nebulizer (SMV), and 3) cyclonic spray chamber and concentric standard nebulizer (CCS) (Fig. 2). The ten adjustment parameters included changes in power, gas flow (plasma, auxiliary, and nebulizer) and time sequence (replicate, stabilization, sample, and rinse). Each set has the changed parameter highlighted in bold (Tables 1 and 2). For both

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

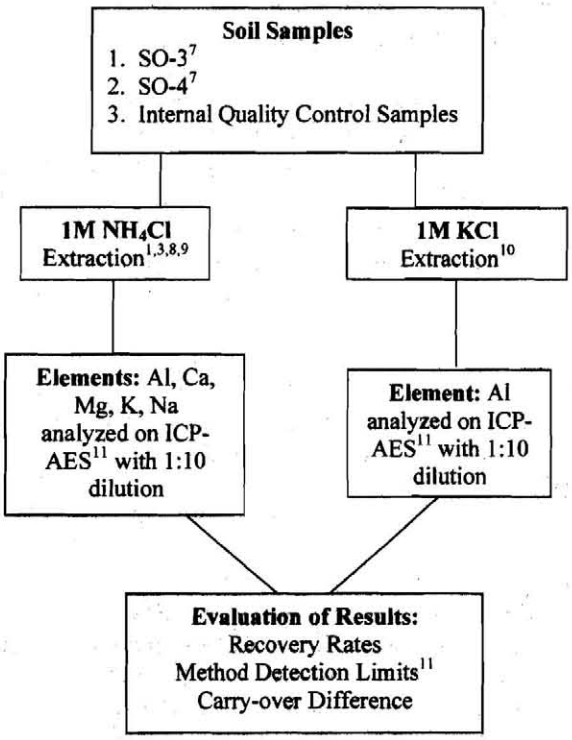

Figure 1. Flow chart for laboratory procedures. Superscripts refer to reference list.

matrices, all solutions were diluted by 1:10, argon saturator was inline, and aluminum was analyzed at 396.152 nm.

RESULTS AND DISCUSSION

Recovery rates (RR), method detection limits (MDL), and carry-over differences (COD) are three ways to evaluate the results. The RR of the quality control samples for all sets were within +/− 10% of complete recovery. The standard deviation bars reveal the sets that had greater variation (NH_4Cl SMV set #1), (KCl TSS and CCS set #10) (Figs. 3 and 4).

MDL represents the lowest concentration that can be detected above method noise. By reviewing the responses to the various parameter changes, one can determine the optimum settings for the method.

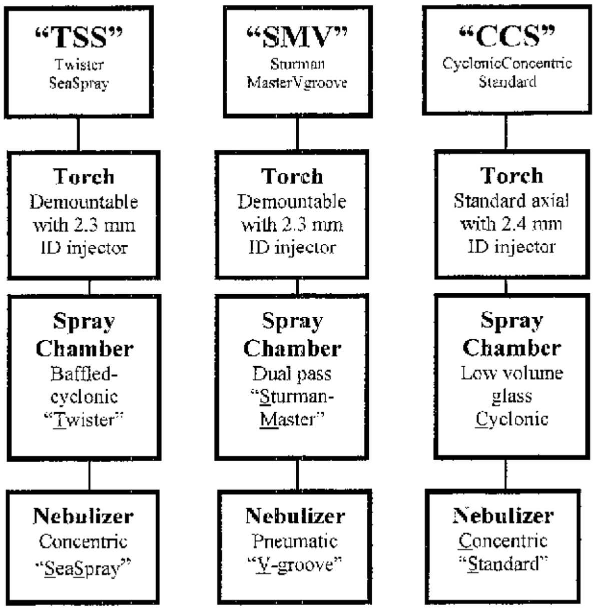

Figure 2. Three hardware setups tested.

COD is a technique to determine if there is any analytical contamination from the previous sample. This technique provides a means to adjust the length of time for sample analysis.

Recovery Rates (RR)

The NH_4Cl extracted soil samples displayed the same responses to the parameter changes. The TSS setup recovery rate increased with the decrease of stabilization time to 15 seconds (set #6). The SMV setup suffered the lowest RR for both samples with the set #8 change, which had the sample uptake set at 30 seconds (Fig. 3).

Increase of auxiliary flow to 2.25 L/min (set #10) caused the KCl extracted soil samples RR to increase dramatically with TSS setup. Meanwhile, the CCS detection increased with set #9 change, which increases the rinse time to 15 seconds (Fig. 4).

Method Detection Limits (MDL)

The changes in the 10 parameters caused a wide fluctuation in the detection limit for the NH_4Cl method. 30% decrease in MDL occurred for the TSS setup with a

Table 1. ICP-AES[12] Parameter Sets for NH_4Cl Matrix[1,3,8,9]

Parameter Set #	1	2	3	4	5	6	7	8	9	10
Changed parameter[a]										
Power (kW)	1.3	**1.2**	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Plasma flow (L/min)	15	15	15	15	15	15	15	15	15	15
Auxiliary flow (L/min)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	**2.25**
Nebulizer flow (L/min)	0.8	0.8	**0.9**	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Replication time (s)	3	3	3	**5**	**10**	3	3	3	3	3
Stabilization time (s)	20	20	20	20	20	**15**	20	20	20	20
Sample uptake (s)	50	50	50	50	50	50	**20**	**30**	50	50
Rinse time (s)	20	20	20	20	20	20	20	20	**15**	20

[a] The changed parameter is designated in bold.

Table 2. ICP-AES[12] Parameter Sets for KCl Matrix[10]

Parameter Set #	1	2	3	4	5	6	7	8	9	10
Changed parameter[a]										
Power (kW)	1.3	**1.2**	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Plasma flow (L/min)	15	15	15	15	15	15	15	15	15	15
Auxiliary flow (L/min)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	**2.25**
Nebulizer flow (L/min)	0.8	0.8	**0.9**	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Replication time (s)	3	3	3	**5**	**10**	3	3	3	3	3
Stabilization time (s)	20	20	20	20	20	**15**	20	20	20	20
Sample uptake (s)	50	50	50	50	50	50	**20**	**30**	50	50
Rinse time (s)	15	15	15	15	15	15	15	15	**20**	15

[a] The changed parameter is designated in bold.

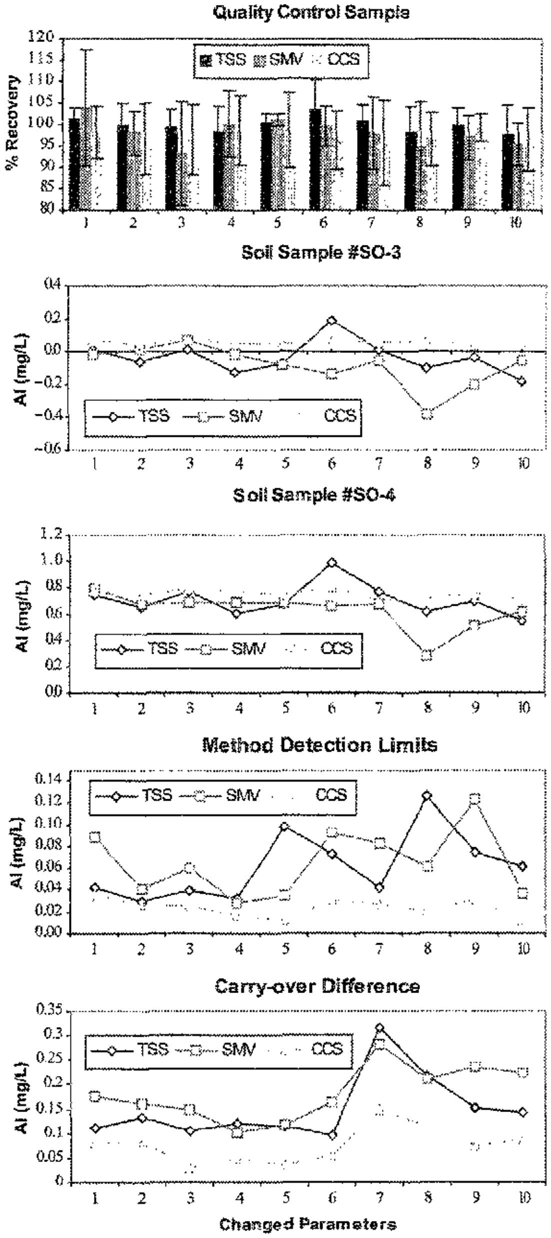

Figure 3. Relationships between hardware setups and changed parameters for NH_4Cl extracted aluminum.

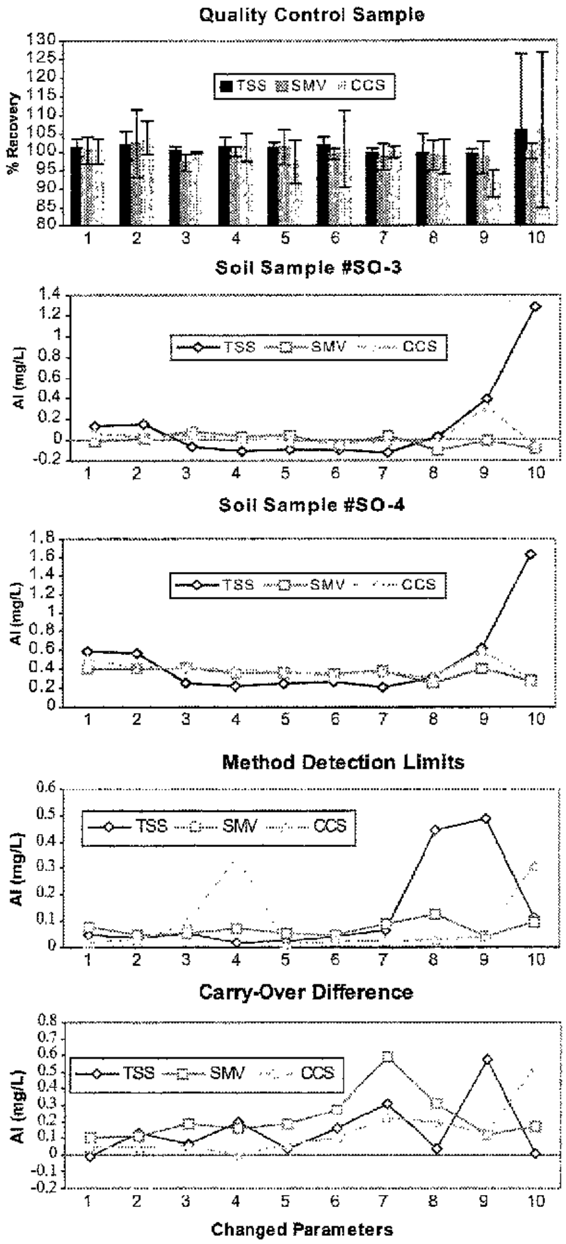

Figure 4. Relationships between hardware setups and changed parameters for KCl extracted aluminum.

decrease in power (set #2). Increase in replicate time (set #4) provided the greatest decrease in MDL for the SMV setup. The CCS setup had the lowest MDL with set #10 changed parameter, which increased of auxiliary flow to 2.25 L/min (Fig. 3).

The method detection limits are more constant for the KCl matrix. The largest change (63%) occurred for the TSS setup with increase in replicate time to 5 seconds (set #4). Increase of rinse time to 20 seconds (set #9) decreased the MDL for the SMV setup by 49%. The change to 10 seconds replicate time (set #5) had the greatest decreasing influence (31%) on the CCS setup (Fig. 4).

Carry-Over Difference (COD)

For the NH_4Cl matrix (Table 1), the parameter set #7, which decreased the sample uptake time from 50 to 20 seconds, caused the greatest change among all three hardware groups (Fig. 3). COD increased 182% for the TSS setup and 82% for the CCS setup.

The KCl matrix (Table 2) was more varied for each of the ICP-AES hardware setups. Parameter set #9 (decrease of rinse time to 15 sec) increased the COD for TSS by the greatest amount. The decrease of sample uptake time to 20 seconds (set #7) increased the carry-over for the SMV setup by five times. The CCS was influenced by the increase of auxiliary flow to 2.25 L/min (set #10) with the COD change of ten times (Fig. 4).

RECOMMENDATIONS

After reviewing the results from the parameter changes, the following recommendations provide the operator with much needed advice. It is important to develop an internal sample similar to the unknowns, since there are no reference materials for extractions.[12] As demonstrated in this paper, it is necessary to test various hardware and parameter sets to obtain optimum results. It is also important to realize that each salt solution can act differently thus requiring unique operational parameters for each matrix. Understanding that results can vary by element is also important. The choice of selecting a specific setup could be based on the results of one element while accepting less optimum results for other elements. Because of all these variables, each instrument requires this testing process before the analyzing any unknowns.

DISCLAIMER

The use of trade, firm, or corporation names in this manuscript is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the USDA Forest Service of any product or service to the exclusion of others that may be suitable.

ACKNOWLEDGMENTS

We are grateful to M. Tansey for his assistance in the laboratory and J. Campbell, K. Dudzik, and T. Luther for their assistance with the paper.

REFERENCES

1. Robarge, W.P.; Fernandez, I. Standard Operating Procedure for Measuring of Exchangeable Bases (Ca, Mg, Na, K) by 1 N NH4Cl. *Quality Assurance Manual for Laboratory Analytical Techniques*; U.S. EPA and USDA Forest Service Response Program: North Carolina State University Acid Deposition Program: Raleigh, NC, 1987; 136–141.
2. Amacher, M.C.; Henderson, R.E.; Breithaupt, M.D.; Seale, C.L.; LaBauve, J.M. Unbuffered and Buffered Salt Methods for Exchangeable Cations and Effective Cation-Exchange Capacity. Soil Sci. Soc. Am. J. **1990**, *54*, 1036–1042.
3. Blume, L.J.; Schumacher, B.A.; Schaffer, P.W.; Cappo, K.A.; Papp, M.L.; Van Remortel, R.D.; Coffey, D.S.; Johnson, M.G.; Chaloud, D.J. Exchangeable Cations in Ammonium Chloride, Section 13. *Handbook of Methods for Acid Deposition Studies. Laboratory Analyses for Soil Chemistry*, EPA/600/4-90/023 National Acid Precipitation Assessment Program; U.S. EPA: Washington, DC, 20460, 1990.
4. Johnson, D. Determination of Metals in Brines by ICP-AES. Varian ICP-10, 1993.
5. Johnson, D. Determination of Metals in a 3% Sodium Chloride (NaCl) Matrix by Axially-Viewed ICP-AES. Varian ICP-19, 1996.
6. Coscione, A.R.; van Raij, B. Revisiting Titration Procedures for the Determination of Exchangeable Acidity and Exchangeable Aluminum in Soils. Commun. Soil Sci. Plant Anal. **1998**, *29* (11–14), 1973–1982.
7. CCRMP: Canadian Certified Reference Materials Project, Mining and Mineral Sciences Laboratories, CANMET, 555 Booth Street, Ottawa, Canada K1A 0G1.
8. Kalra, Y.P.; Maynard, D.G. Cation Exchange Capacity and Exchangeable Cations. *Methods Manual for Forest Soil and Plant Analysis*, Information Report NOR-X-319; Forestry Canada: Edmonton, Alberta, Canada, 1991; 84–94.

9 Johnson, D.W.; Richter, D.D.; Lovett, G.M.; Lindberg, S.E. The Effects of Atmospheric Deposition on Potassium, Calcium, and Magnesium Cycling in Two Deciduous Forest. Can. J. For. Res. **1985**, *15*, 773–782.

10 Thomas, G.W. Exchangeable Cations. In *Methods of Soil Analysis, Part 2—Chemical and Microbiological Properties*, 2nd Ed.; Page, A.L., Ed.; American Society of Agronomy: Madison, WI, 1982; 159–165.

11 *Vista CCD Simultaneous, Axial Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) Handbook*; Varian Australia Pty., Ltd: Victoria, Australia, 2000.

12 Kennedy, V.H.; Rowland, A.P.; Parrington, J. Quality Assurance for Soil Nutrient Analysis: A Case Study. Commun. Soil Sci. Plant Anal. **1994**, *25* (9–10), 1605–1627.