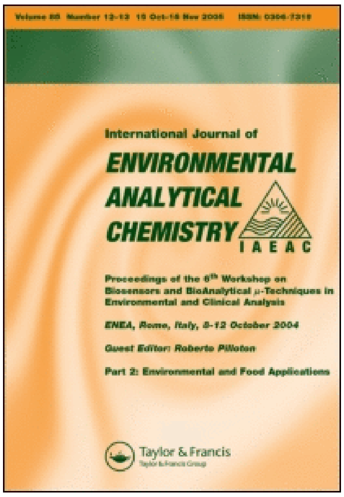

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DETERMINATION OF CARBON, NITROGEN AND SULFUR IN SOILS, SEDIMENTS AND WASTES: A COMPARATIVE STUDY

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The determination of low levels ($<1\%$) of total carbon and nitrogen in soils, sediments and solid wastes is made fast using an automated elemental NCS analyzer (Carlo Erba NA-1500). The recoveries of total *N* obtained were similar with either the elemental analyzer or the Kjeldahl digestion method used. The recoveries and precision of the TC, TOC data were better and more predictable using the elemental analyzer than the wet digestion procedure used in this study. Acid pre-treatment prior TOC determinations using the NCS analyzer resulted in lower total *N* recoveries. The determination of *S* in the same materials using this analyzer is not recommended due to low recoveries and poor precision.

KEY WORDS: Organic carbon, soil, sediment, solid waste, elemental analyzer.

INTRODUCTION

Reliable quantitative data on the amounts of nitrogen (N), total and organic carbon (TC, TOC), and sulfur (S) in environmental materials (wastes, sediments and soils) are important. These data are necessary to evaluate land treatability potential, degree of contamination and potential fertility levels of soils, sediments and wastes. The use of total elemental analyzers to determine N, C and S in soil samples has already been suggested and reviewed.[1] However, this method of analysis, when used for the simultaneous determinations of low levels ($<1\%$) of N, C and S in soils, sediments and solid waste samples, needs further evaluation.

The determination of TOC in soils has traditionally been carried out using the dichromate-sulfuric acid digestion procedures by Walkley and Black.[2] The recoveries of organic carbon using these methods are usually much less than 100% and cannot be predicted. In the case of soils recoveries have been found to vary from 75–86%[1,2] depending on the soils and methods used. Dichromate-sulfuric acid methods which include heating (such as Allison and Mebius) have shown to provide good agreement with dry combustion procedures but are still prone to false positive and negative values when significant amounts of oxidizable or reducible constituents (Cl^-, MnO^2, Fe^{2+}) are present.[1] Limited information is available on the performance of elemental analyzers used for the analysis of sediments and wastes.

The determination of total N in soils is traditionally done using the Kjeldahl wet digestion technique. This method and its variations[3] generate significant amounts of toxic waste (sulfuric acid with either Se or Hg). Recoveries of N using this method are predictable but do not include any of the nitrate-N present unless a sample preparation (nitrate reduction) is done prior to the wet digestion.[3] High temperature combustion methods to determine N in plant tissue and chemicals of known N composition have been tested and deemed acceptable.[4]

The determination of total S in soils presents a formidable challenge when any of the traditional methods is used, as they require an oxidation and a reduction step of the element prior to quantification.[5] These methods are long and complicated and also generate significant amounts of acid and metal-containing solutions.

The Carlo Erba NA-1500 analyzer has been used successfully for the simultaneous determination of N, C and S in crude oils[6] and chemicals containing high levels ($>1\%$) of each of these three elements. However, the performance of this unit and suitability for the simultaneous analysis of N, C and S in soils, wastes and sediments with low ($<1\%$) N, C and S levels and refractive matrices, remain to be evaluated.

The objectives of this research were; (1) to compare recoveries and precision of the Carlo Erba elemental analyzer with those obtained using wet digestion methods, and (2) to determine the lower limits of detection of this unit.

MATERIALS AND METHODS

1) N-C-S analyzer, Carlo Erba model NA-1500.
2) Integrator, Varian 4290.
3) Balance, micro-analytical Cahn model C-30.

The NCS NA-1500 unit was operated according to the manufacturer specifications in the N-C-S simultaneous analysis mode. That is, manufacturer specified instrument conditions, ultrapure gases and manufacturer supplied chemicals were used throughout the study. Briefly, this unit operates on the Dumas combustion principle. It has a quartz tube packed with a layer granular ultrapure tungsten(VI) oxide and a layer of reduced copper wires. The tube is heated to 1000 °C while ultrapure He gas is passed through the tube at a rate of about $100\,\mathrm{cc\,min^{-1}}$. A finely ground sample (3–50 mg) is weighed to the nearest 0.001 mg into a tin cup using a micro-balance. The enclosed sample is introduced into the combustion tube with the aid of a carousel and timed to coincide with a pulse (20 cc) of ultrapure O_2 gas. The combination of the tin and tungsten oxide catalysts, O_2 and high temperature is designed to convert all forms of N to N_2, C to CO_2, and S to SO_2 gases. Subsequently, the excess O_2 reacts with the Cu wire. Also, the excess moisture is removed from the gas stream with an ascarite trap. The remaining gases are separated with the aid of a Porapak Q gas-solid chromatography column and measured and quantified with a thermal conductivity detector and a peak integrator. This entire process takes seven minutes and is fully automated. Traditional methods for sample preparation and analyses were also used. A modified macro-Kjeldahl (with Pope mixture No. 5, Hg based) digestion procedure was used, as described by Bremner and Mulvaney,[3] without the nitrate reduction step. Ammonia was quantified in TKN digests using a colorimetric procedure by Baethgen.[10] Total organic carbon was measured using the Allison method, as described by .Nelson and Sommers.[2] Total S determinations were done using a combination of sodium and bicarbonate dry ashing and ion chromatography.[5,7]

Tables 1–6 list all of the materials analyzed during this study. Some but not all of the reference materials have certified values for N, C, or S. All of the samples with certified concentrations of N, C or S came from the Canada Centre for Mineral and Energy Technology (CANMET), the National Institute of Standards and Techology (NIST) and Carlo Erba Instruments. The SMA-1 soil is a sandy clay loam agricultural top soil from Arizona. The Ava soil is an Alfisol (B-horizon material) with a silty clay loam texture from Illinois. The R.H. soil is a Houston black clay soil from an industrial sludge land treatment farm. The C.W. soil is a clay soil from an oilfield waste land treatment farm in the Louisiana. The sludge sample came from one of the sewage treatment plants in Tucson AZ. The graphite was supplied by the department of geosciences of the University of Arizona and had a purity of better than 99.9% C. The barite used was a Reagent grade chemical from Mallinckrodt and had a $BaSO_4$ purity of 99.7% The sulfamic acid used was from Fisher Scientific with a certified purity of 99.8%. The potato and onion plant tissues were obtained by the Far West Soil and Plant Testing Workgroup 1989 Round Robin.

In order to remove inorganic carbon forms, sediments and soils were treated with a solution of 10% H_3PO_4 at a soil:solution ratio of 1:5 or more, as needed to eliminate any effervescence and bring the pH of the slurry to less than 6.

All of the materials were oven dried either at 105 °C (soils, sediments and chemicals) and stored in dissectors. All non-certified materials were also reduced to a size of <100 microns using a Spex ball mill. These steps are considered necessary for optimum sample bulking and are crucial in insuring good precision of data.[7,9] It should be noted that the sample sizes used in the wet digestion/ashing procedures and the elemental analyzer ranged from 0.1–1 g and 3–50 mg, respectively.

RESULTS AND DISCUSSION

Quality Control

The elemental analyzer was calibrated daily using manufacturer standards. In order to check both recoveries and precision, two or more certified materials were analyzed with each set of ten environmental samples. Similarly, the wet digestion procedures were checked daily with the aid of blanks and certified standards.

Tables 1, 2 and 3 present the N, C, and S results for materials which were used throughout the analyses of the soils, sediments and wastes. These materials were used to check recoveries and precision. In general, both the recoveries and precision data of these samples were superior to the environmental samples analyzed during this study. This is in part due to the fact that most of these

Table 1 Nitrogen data for quality control materials

Name	*Origin*	*Reference values*				*NA-1500 data*					*TKN data*				
		N (%)	*Std.*	*CV* (%)	*n*	*N* (%)	*Std.*	*CV* (%)	*Rec.* (%)	*n*	*N* (%)	*Std.*	*CV* (%)	*Rec.* (%)	*n*
Graphite[a]	Geo. Dept.	NA	NA	NA	NA	0.086	0.02	20.33		4					
Oyster tissue 1566[a]	NIST	NA	NA	NA	NA	6.55	0.133	1.73		4	4.91	0.08	1.54		4
Tomato lea. 1573[a]	NIST	5.0	NA	NA	NA	4.94	0.139	2.81	98.72	17	4.60	0.10	2.21	91.74	4
Pine needles 1375[a]	NIST	1.2	NA	NA	NA	1.12	0.062	5.51	93.40	8	1.48	0.03	2.48	97.98	4
Potato tissue[a]	Farr. West PEP	2.49	0.20	8.0	47	3.33	0.11	3.29	128.8	8	2.57	0.06	2.48	103.2	3
Onion tissue[a]	Farr. West PEP	2.34	0.134	5.7	47	2.3	0.07	3.03	98.22	8	2.36	0.15	7.10	100.9	4
Sulfanilammide[b]	Carlo Erba	16.27	NA	NA	NA	16.18	0.357	2.21	99.42	16					
5-Chloro-4-hydroxy-3-methoxy-benzylisothiourea phosphate[b]	Carlo Erba	8.13				8.1	0.19	2.34	99.65						
	Mean recoveries								103.03					98.45	

[a] Indicates value not certified or from a round robin.

[b] Indicates value certified.

(NA) Indicates Not Applicable (precision data available only) or Not Available.

Note: All reference values listed with exact number of significant digits from sources.

Table 2 Carbon data for quality control materials

	Origin	Reference values		NA-1500 data				
		C (%)	Std., CV, n	C (%)	Std.	CV (%)	Rec. (%)	n
Graphite[a]	Geo. Dept.	100.0	NA	99.66	2.74	2.75	99.64	4
Oyster tissue 1566[a]	NIST	NA	NA	47.66	0.1952	0.41	NA	4
Tomato lea. 1573[a]	NIST	NA	NA	38.66	0.343	0.89	NA	17
Pine needles 1375[a]	NIST	NA	NA	51.04	0.312	0.61	NA	8
Potato tissue[a]	Farr. West PEP	NA	NA	32.01	0.244	0.76	NA	8
Onion tissue[a]	Farr. West PEP	NA	NA	38.24	0.099	0.26	NA	8
Sulfanilammide[b]	Carlo Erba	41.84	NA	42.42	0.619	1.46	101.4	16
5-Chloro-4-hydroxy-3-methoxy-benzylisothiourea phosphate[b]	Carlo Erba	31.35	NA	31.26	0.56	1.81	99.69	8
	Mean recoveries						100.2	

[a] Indicates value not certified or from a round robin.

[b] Indicates value certified.

(NA) Indicates Not Applicable or Not Available.

Note: All reference values listed with exact number of significant digits from sources.

quality control samples were either organic chemicals or organic tissues. Pure graphite was used to check the recoveries of total C, with an overall recovery of better than 99.5% and a %CV of 2.7%. Barium sulfate was used to check S recoveries. The results indicate that this very stable crystalline form of SO_4^{2-} does not recover well with either the NCS analyzer (recovery = 73.3% and %CV = 9.6% or with the dry ashing method (recovery = 0.8%). However, sulfur recoveries, obtained from the analysis of the two S certified organic chemicals and the oyster tissue, were >98% and >90%, respectively with acceptable %CVs.

Total Nitrogen Recoveries

The initial quality control and recoveries check of total N for the NCS analyzer were done with plant tissue and biological samples of known N content. As seen in Table 1, most of the recoveries obtained with the NCS analyzer were within 5% of the certified values. Notable exceptions were the pine needles and potato tissues. The pine needles material had lower than expected N recoveries (93%) and a CV higher than 5%. The potato tissue sample had a reported TKN value of 2.49% which did not include the NO_3-N concentration of about 1%. Therefore, the analysis of the potato tissue using the NCS analyzer produced N recovery close to the sum of these two values (3.33%N), see Table 1.

The total N recovered from soils, sediments and wastes was very similar for both the NCS analyzer and the wet digestion (Kjeldahl) methods, see Table 5. However, the data from the wet digestion procedure had somewhat higher variances (%CV) than the NCS analyzer data.

In general, the variances (%CV) increased significantly (>5%CV) for soil samples with N levels below 0.1%. Also, recoveries of N were significantly lower (>5% reduction) for the acid treated samples when determined with both the

Table 3 Sulfur data for quality control materials

Name	Origin	Reference values				NA-1500 data					Ashing data				
		S (%)	Std.	CV (%)	n	S (%)	Std.	CV (%)	Rec. (%)	n	S (%)	Std.	CV (%)	Rec. (%)	n
Barite[b]	Mallinck.	13.77	NA	NA	NA	10.56	1.014	9.6	73.32	4	0.109	0.005	4.67	0.79	4
Oyster tissue 1566[a]	NIST	0.76	NA	NA	NA	0.690	0.03	4.36	90.4	4	0.642	0.008	1.23	88.1	8
Tomato lea. 1573[a]	NIST	NA	NA	NA	NA	0.340	0.097	28.46	NA	15	0.550	0.010	0.92	NA	4
Pine needles 1375[a]	NIST	NA	NA	NA	NA	<0.05			NA		0.104	0.003	2.64	NA	4
Potato tissue[a]	Farr. West	0.2029	0.046	22.4	47	0.032	0.048	149	NA	8	0.163	0.001	0.79	80.33	4
Onion tissue[a]	Farr. West	0.535	0.134	25.0	47	0.328	0.058	17.7	51.04	8	0.505	0.02	4.03	95.9	4
Sulfanilammide[b]	Carlo Erba	18.62	NA	NA	NA	18.323	0.423	2.31	98.37	14	NA			NA	
5-Chloro-4-hydroxy-3-methoxy-benzylisothiourea phosphate[b]	Carlo Erba	9.30	NA	NA	NA	9.16	0.793	8.65	98.19	7	NA			NA	
Sulfamic acid[b]	Fisher sci.	32.99	NA	NA	NA	NA					29.51	0.68	2.31	92.2	4
	Mean recoveries								82.26					89.13	

[a] Indicates value not certified or from a round robin.

[b] Indicates value certified.

(NA) Indicates Not Applicable (precision data available only) or Not Available.

Note: All reference values listed with exact number of significant digits from sources.

Table 4 Nitrogen data for soils, sediments and wastes

Name	*Origin*	*Reference values*				*NA-1500 data*					*TKN data*				
		N (%)	*Std.*	*CV* (%)	*n*	*N* (%)	*Std.*	*CV* (%)	*Rec.* (%)	*n*	*N* (%)	*Std.*	*CV* (%)	*Rec.* (%)	*n*
SO-3 ref. soil[a]	CANMET	0.02	NA	23.1	22	0.012	0.002	20.61	45.82	8	0.011	0.005	45.89	38.9	4
SO-3 ref. soil, tr.						0.011	0.001	5.5	41.1	4					
SO-4 ref. soil[a]	CANMET	0.4	NA	2.3	30	0.381	0.009	2.3	95.17	8	0.415	0.036	8.79	103.4	4
SO-4 ref. soil, tr.						0.343	0.003	0.84	85.75	4					
Coal material bit.[b]	NIST	1.56	0.07	NA	NA	1.53	0.017	1.14	97.9	4	1.50	0.034	2.28	96.4	4
Coal material bit., tr.						1.35	0.01	0.64	86.54	3					
Buffalo river sedi.[a]	NIST	NA				2	0.022	4.74	NA	9	0.169	0.009	5.28	NA	4
Buffalo river sedi., tr.						0.166	0.001	0.302	NA	4					
SMA-1 soil[a]	SWPAL	NA				0.078	0.001	1.22	NA	4	0.079	0.01	12.12	NA	4
SMA-1 soil, tr.		NA				0.072	0.002	1.13	NA	4	0.071	0.001	3.96	NA	4
C.W. soil[a]	LA	NA				0.051	0.001	2.1	NA	8	0.044	0.001	5.18	NA	4
C.W. soil, tr.		NA				0.044	0.001	2.4	NA	8	0.048	0.001	2.95	NA	4
R&H soil[a]	TX	NA				0.457	0.008	1.8	NA	4	0.409	0.01	2.99	NA	4
R&H soil, tr.		NA				0.293	0.003	1.13	NA	4	0.288	0.03	9.79	NA	4
Eva soil[a]	IL	NA				0.037	0.000	0.85	NA	4	0.039	0.002	6.33	NA	4
Eva soil, tr.		NA				0.034	0.000	0.86	NA	4	0.034	0.003	8.23	NA	4
Sludge, Tucson[a]	AZ	NA				2.34	0.027	1.16	NA	4	2.12	0.03	1.25	NA	3
Sludge, Tucson, tr.		NA				1.96	0.55	2.78	NA	4	1.86	0.17	9.2	NA	3
	Mean recoveries								91.34					99.9	

[a] Indicates value not certified or from a round robin.

[b] Indicates value certified.

(NA) Indicates Not Applicable (precision data available only) or Not Available.

Note: All reference values listed with exact number of significant digits from source "Tr" indicates material treated with 10% H_3PO_4 solution.

Table 5 Carbon data for the soils, sediments and wastes

Name	*Origin*	*Reference values*				*NA-1500 data*					*Allison data*				
		C (%)	*Std.*	*CV* (%)	*n*	*C* (%)	*Std.*	*CV* (%)	*Rec.* (%)	*n*	*TOC* (%)	*Std.*	*CV* (%)	*Rec.* (%)	*n*
SO-3 ref. soil[a]	CANMET	6.6	NA	0.6	31	6.81	0.015	0.22	103.2	8	3.26	0.235	14.36	NA	7
SO-3 ref. soil, tr.						2.71	0.02	0.55	NA	4					
SO-4 ref. soil[a]	CANMET	4.4	NA	1.0	38	4.44	0.044	0.99	100.8	8	2.98	0.12	4.02	NA	4
SO-4 ref. soil, tr.						3.90	0.02	0.44	NA	4					
Coal material bit.[b]	NIST	78.11	0.37	NA	NA	76.38	0.484	0.63	97.80	4	48.97	2.61	5.33	NA	11
Coal mat. bit., tr.						63.93	1.07	1.67	NA	3					
Buffalo River sed.[b]	NIST	3.348	0.016	NA	NA	3.52	0.423	12.01	104.5	9	1.80	0.18	9.81	NA	8
Buffalo River sedi., tr.						2.29	0.006	0.253	NA	4					
SMA-1 soil[a]	SWPAL	NA				1.29	0.017	1.33	NA	4	0.789	0.079	10.1	NA	6
SMA-1 soil, tr.		NA				0.810	0.01	1.01	NA	4					
C.W. soil[a]	LA	NA				2.48	0.047	1.89	NA	8	1.45	0.02	1.32	NA	4
C.W. soil, tr.		NA				1.69	0.071	4.22	NA	8					
R&H soil[a]	TX	NA				3.4	0.059	1.72	NA	4	2.32	0.058	2.49	NA	6
R&H soil, tr.		NA				2.52	0.025	0.99	NA	4					
Eva soil[a]	IL	NA				0.283	0.011	3.96	NA	4	0.200	0.018	8.9	NA	10
Eva soil, tr.		NA				0.246	0.005	1.90	NA	4					
Sludge, Tucson[a]	AZ	NA				20.13	0.325	1.61	NA	4	14.33	0.74	5.18	NA	8
Sludge, Tucson, tr.		NA				16.36									
	Mean recoveries								101.5					NA	

[a] Indicates value not certified or from a round robin.

[b] Indicates value certified.

(NA) Indicates Not Applicable (precision data available only) or Not Available.

Note: All reference values listed with exact number or significant digits from source "Tr" indicates material treated with 10% H_3PO_4 solution.

Table 6 Sulfur data for soils, sediments and wastes

Name	*Origin*	*Reference values*				*NA-1500 data*					*Ashing data*				
		S (%)	*Std.*	*CV* (%)	*n*	*S* (%)	*Std.*	*CV* (%)	*Rec.* (%)	*n*	*S* (%)	*Std.*	*CV* (%)	*Rec.* (%)	*n*
SO-3 ref. soil[b]	CANMET	0.015	0.003	NA	17	<0.05			30		0.019	0.0001	7.44	116.6	4
SO-3 ref. soil, tr.						<0.05			30						
SO-4 ref. soil[b]	CANMET	0.044	0.02	NA	17	<0.05			15		0.042	0.001	2.29	96.71	4
SO-4 ref. soil, tr.						<0.05			15						
Coal material bit. 1	NIST	1.89	0.06	NA	NA	1.52	0.1	6.3	77.80	4	1.82	0.02	1.00	97.40	4
Coal mat. bit. 1632b, tr.						1.32	0.082	6.21	69.84	3					
Buffalo River sed.[a]	NIST	0.4	NA	NA	NA	0.206	0.029	14.15	51.50	7	0.344	0.008	2.43	89.50	7
Buffalo River sed. 2704, tr.						0.224	0.032	14.18	56.00	4					
SMA-1 soil[a]	SWPAL	NA				<0.05			NA		0.028	0.001	2.1	NA	4
SMA-1 soil, tr.		NA				<0.05			NA		0.026	0.000	0.000	NA	4
C.W. soil[a]	KWBA	NA				0.185	0.09	49.11	NA	8	0.282	0.01	3.38	NA	4
C.W. soil, tr.		NA				0.653	0.05	7.49	NA	8	0.276	0.011	3.87	NA	4
R&H soil[a]	KWBA	NA				0.079	0.01	11.61	NA	4	0.155	0.006	3.76	NA	4
R&H soil, tr.	KWBA	NA				0.087	0.004	5.27	NA	4	0.103	0.002	1.59	NA	4
Eva soil[a]	SWS	NA				<0.05			NA		0.016	0.016	27.61	NA	4
Eva soil, tr.	SWS	NA				<0.05			NA						
Sludge, Tucson[a]	SWS	NA				0.659	0.004	0.60	NA	4	0.809	0.010	1.20	NA	4
Sludge, Tucson, tr.	SWS	NA				0.576	0.36	61.95	NA	4	0.652	0.006	0.88	NA	4
	Mean recoveries								43.14					100.0	

[a] Indicates value not certified or from a round robin.

[b] Indicates value certified.

(NA) Indicates Not Applicable (precision data available only) or Not Available.

Note: All reference values listed with exact number of significant digits from source "Tr" indicates material treated with 10% H_3PO_4 solution.

NCS analyzer and the Kjeldahl method. The reason for the decrease (volatilization) in N levels in H_3PO_4 treated soil samples is not clear and merits further study.

TC and TOC Recoveries

Soils, sediments and wastes have two forms of carbon of interest. The inorganic fraction (TIC) usually associated with carbonates and bicarbonates. This fraction is acid reactive and will readily form CO_2 when the pH drops below 4. The organic fraction (TOC) is typically associated with the plant residues, humic/fulvic acids organic residues and natural or synthetically manufactured materials. However, other forms of carbon such as charcoal and graphite may also be found in soils which may or may not be recovered by wet TOC procedures. Total carbon (TC) includes both TIC and TOC plus other highly reduced forms of C such as graphite. Soils with pH values above 7 may contain significant amounts of TIC and require pre-treatment with acid prior to the determination of TOC.

The initial calibration, organic carbon recoveries and quality control checks on the NCS analyzer were done using various plant materals, a biological material and two reagent grade chemicals. All of these materials had organic carbon levels above 30%. Both the recoveries and precision of the TOC data obtained with these materials were >95% and <5%CV, respectively.

The TC recoveries of the Reference SO-3 and SO-4 Canadian soils using the NCS analyzer were well within 5% of the certified values with a coefficient of variance (%CV) better than 1%, see Table 4. The H_3PO_4, treatment of these two soils produced TOC significantly above and below the values obtained using the wet oxidation procedure (Allison) for the SO-3 and SO-4 soils, respectively. It is likely that the very high levels of carbonates found in the SO-3 soil interfered in the wet digestion procedure, as only the SO-3 soil contained had significant amounts of carbonates/bicarbonates (>3% as C). Total carbon recoveries of the coal material and river sediment were also within 5% of the certified values using the NCS analyzer. The H_3PO_4, treatment of these two materials also produced significantly lower C values, which indicated the presence of significant amounts of inorganic C. Also, the TOC recoveries of the wet oxidation procedure were more than 20% lower than those obtained using the NCS analyzer. The wet digestion procedure and the total organic carbon recoveries of the treated SMA-1, C.W., R.H. and Ava soils, and the Tucson sludge ranged from 81% to 97% below the levels recovered with the NCS analyzer. Since these materials did not have certified TC or TOC values, they were used for comparative purposes as well as to check the precision of each method. The TC recoveries obtained on the above materials showed significant TIC levels with the expected exception of the Ava soil which is an acidic soil (pH ~ 5).

In general, the TOC data precision was higher with NCS analyzer than with the wet oxidation procedure at given level. However, as expected both procedures showed decreased precision with lower levels of carbon. The TC precision and accuracy (recoveries) and TOC precision data generated by the NCS analyzer was excellent (<2%CV). The wet oxidation (Allison) methods produced significantly lower (at the 0.05 confidence level) TOC levels by about 2–20% with the exception of the SO-3 soil which had TIC levels (>3%) and may not have been pre-treated properly during the wet oxidation procedure. These findings are consistent with sediment TOC data recently reported by Lee and Macalady[10] comparing the wet oxidation procedure with high temperature and colorimetric titration method.

Total S Recoveries

As with the other two elements, initial calibrations for S recoveries were done with certified chemicals. The recovery checks of the sulfanilamide and thiourea reagents was better than 98% but with an overall variance as high as 8.7%CV, see Table 3. However, the recoveries of S from plant tissue samples using the NCS analyzer had very poor precision (as high as 28%CV) and were significantly below the mean values reported in Table 1 for the potato and onion tissue, see Table 3. The S data for the potato tissue could not be quantified due to its unacceptable precision and low recovery. The range of plant tissue sample weights used in this study was 5–20 mg.

In the case of the dry ashing procedure, the recoveries of S in sulfamic acid were about 93% with a CV of 2.3% and the recoveries of S from potato and onion tissues were 80 and 96%, respectively, with CVs 4% or less. It should be noted that the potato and onion tissue S values reported in Table 3 came from a Round Robin study which reported variances in the data in excess of 22%.

Based on the NCS analyzer total S data, most of the soils used in this study contained S levels well below 0.1%. The R.H. soil was determined to have from 0.08% to 0.09% sulfur with poor precision (>10%CV), see Table 6. The C.W. soil had measurable S levels ranging from about 0.19 to 0.65%, with and without phosphoric acid treatment. The varying S levels in the C.W. soil may be in part due to the presence of large levels of barite (>1%) from oilfield wastes. Also, the precision obtained in the analysis of this soil using the NCS analyzer was unacceptably high. A similar pattern of varying S recoveries and high %CV was observed for the Tucson sludge sample. Sulfur recoveries in the rest of the soils used in this study could not be tested since the unit detection limit was found to be about 0.05% using maximum sample size of 50 mg. The S recovery of the barium sulfate chemical was substantially below the expected values (73.3%). This low recovery may be due to the fact that barite is a highly stable refractory compound which may not be efficiently reduced via the Dumas process.

The total S data generated using the dry ashing procedure had very high precision (CV=4% or less) and high levels (>95%) of S recovery, specially for samples with certified S values, see SO-3 and coal material, Table 6. Soil samples with less than 0.02% S had high %CV (>10%), making the results unacceptable, see SO-3 and Ava soils, Table 6. Also S recoveries from barium sulfate were more than two orders of magnitude below the certified value, see Table 3. This is to be expected since the solubility of barium sulfate is very low ($K_{sp} \sim 1 \times 10^{-10}$), making the sulfate ion unavailable for determination using ion chromatography.

SUMMARY AND CONCLUSIONS

The total N values and quality for the data generated with the NCS analyzer were equal in accuracy and somewhat better in precision to those obtained from the TKN wet digestion procedure. The limits of detection for total N were determined to be at or near those claimed by the manufacturer (0.01%) with acceptable precision.

In general, both the recovery and precision of TOC using the NCS analyzer were found to be significantly higher than the wet oxidation (Allison) procedure when appplied to soil, sediment and waste samples. The TC concentrations determined with the NCS analyzer also had high precision and accuracy and conformed well with certified values.

Using the NCS analyzer, both precision and recoveries of C and N in the analysis of soils, sediments and wastes were unaffected by the sample size within a range of 3–50 mg. However, as with the wet digestion procedures, the variances tended to increase with decreasing N, and C concentrations.

The NCS analyzer S detection limit was found to be 3–5 times higher than those claimed by the manufacturer (0.01%). This analyzer did not generate reliable quality data on total sulfur data from soils, sediments or wastes or even plant tissue samples with S concentrations below 1%. However, both precision and accuracy data were acceptable when tested using two certified organic reagents with S concentrations well above 1%. Total S data generated with the dry ashing-IC procedure had very high precision ($<4\%$CV) for samples containing more than 0.02% S and general recoveries better than 90% for most of the certified materials tested including soils and sediments.

Acid (H_3PO_4) pre-treatment of soil, sediment and waste samples to eliminate carbonates and bicarbonates to determine both total N and TOC simultaneously in soils, sediments and wastes produced significantly lower total N recoveries.

The use of this NCS analyzer for total sulfur in soils, sediments and wastes cannot be recommended due to erratic S recoveries.

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