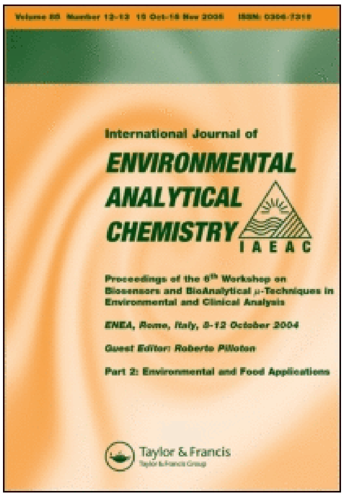

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João M. M. Leitão[a]; Felisbela S. Costa[a]; Filip M. G. Tack[b]
[a] Laboratory of Analytical Instrumental Methods, Faculty of Pharmacy, University of Coimbra, Coimbra, Portugal [b] Department of Applied Analytical and Physical Chemistry, Ghent University, Ghent, Belgium

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DETERMINATION OF TOTAL SULFUR IN SOILS AND PLANTS BY AN AUTOMATED DRY COMBUSTION METHOD

JOÃO M.M. LEITÃO[a*], FELISBELA S. COSTA[a] and FILIP M.G. TACK[b]

[a]Laboratory of Analytical Instrumental Methods, Faculty of Pharmacy, Couraça dos Apostólos 51, University of Coimbra, P-3000 Coimbra, Portugal and [b]Department of Applied Analytical and Physical Chemistry, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium

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Determination of total sulfur in environmental samples can be accomplished using automated dry combustion techniques. The analytical performance of an elemental analyzer (CE Instruments) was compared with a method involving dry ashing followed by ion chromatographic detection of sulfate (IC). Samples included certified reference materials, confirmation materials with a known content of sulfur, and several soils and plants. There was a close agreement between both methods. Superior accuracy, precision and detection limits were obtained using the dry combustion method. Current results suggest that the automated dry combustion technique has developed into an adequate method for the determination of the relatively low total sulfur contents commonly encountered in soils and plants.

Keywords: Total sulfur; elemental analyzer; soil; compost and plant

INTRODUCTION

Sulfur is one of the main elements in the biosphere. Accurate and rapid determination of sulfur is important in soil and plant research and in agricultural and environmental monitoring programs. Many methods have been proposed for the determination of total sulfur in soils and plants[1,2]. Usually the various forms of sulfur are converted, either by oxidation to sulfate or by reduction to sulfide. These methods are always time- consuming, complicated and generate significant amounts of acid and/or metal wastes. For the determination of sulfide no procedure has been entirely satisfactory except for the colorimetric method using

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[*] Corresponding author. Fax: +351 239 852 569. E-mail: leitaoj@ci.uc.pt

methylene blue[1]. In contrast, several reliable methods are available for the determination of sulfate. These include gravimetry, turbidimetry and nephelometry, titrimetry, colorimetry, ICP-AES and chromatography[1,2].

Since the eighties, automated elemental analyzers optimized for the automatic determination of sulfur in environmental matrices have become available. Their advantage lies in their relative simplicity of use, speed and convenience. An additional advantage is that much lower amounts of waste are produced than by using conventional wet-chemistry methods.

Earlier equipment for automated elemental analysis appeared unsatisfactory for research that requires accurate and precise determination of total sulfur[1,2,3]. While accuracy and precision were found acceptable for carbon and nitrogen, Artiola[3] concluded that "the use of this NCS analyzer for total sulfur in soils, sediments and wastes cannot be recommended due to erratic sulfur recoveries". With a different instrument, Soon and al.[2] obtained a good reproducibility but a low accuracy and recovery in plants with relatively high sulfur contents. The objective of this study was to re-evaluate the performance of an automated elemental analyzer (CE Instruments). Special reference is made to the work of Artiola[3] who evaluated the performance of an earlier version of this equipment.

EXPERIMENTAL

For the determination of sulfur by dry combustion a CE Instruments model 2100 (CE Instruments, Milano, Italy) was used in the NCS configuration. The NCS analyzer was operated according to the manufacturer's specifications. Ultrapure gases and manufacturer supplied standards were used throughout. The unit operates on the Dumas combustion principle[1]. The elemental analyzer was calibrated using standards and certified reference materials for the content of sulfur.

Samples between 10 to 80 mg for soils, 6 mg for plants and 0.5 mg for confirmation materials were weighed to the nearest 0.001 mg into a pure tin container. About 10 mg of vanadium pentoxide was added to ensure complete oxidation of all forms of sulfur. The analytical process proceeds as following. Samples are introduced automatically into a quartz combustion reactor heated at 1000°C. At the same moment, 20 ml of ultrapure O_2 is also introduced. The heat generated by the exothermic tin oxidation reaction increases the local temperature briefly to 1800°C, which causes quantitative combustion of the sample. Combustion gasses are carried with a flow of ultrapure helium at a flow rate of 140 ml/min and are passed over a column packed with a layer of granular tungsten oxide (WO_3) and a layer of reduced copper wires. This setup is designed to convert all forms of N to N_2, C to CO_2 and S to SO_2 gases. The excess of O_2reacts with the Cu wire. The gasses are subsequently carried over an "Anhydrone" trap to absorb moisture and passed to a GC column and thermal conductivity detector for separation and detection. This analysis lasts for seven minutes and is fully automated.

A method for total sulfur analysis that involves dry ashing[1] followed by sulfate detection with ion chromatography[4,5,6] was also applied. An amount of material depending on the expected content of sulfur (between 50 to 200 mg for soils and plants and around 10 mg for chemicals) was ashed with 0.25 g $NaHCO_3$ and 0.01 g Ag_2O during 3 hours at 550°C. The ash was boiled in 50 mL of carbonate/bicarbonate buffer (2.6 mmol L^{-1} $Na_2CO_3 + 2.4$ mmol L^{-1} $NaHCO_3$) during 3 hours under reflux. Sulfates in the extract were analyzed by ion chromatography (Dionex 2000i/SP, Dionex Corporation, Sunnyvale, CA). Aqueous standard solutions of sulfate (0.1, 0.5, 5 and 10 mg/l), freshly prepared using reagent grade anhydrous sodium sulfate (UCB, Brussels), were used for calibration.

Quality control materials used are listed in Table I. Besides, a variety of soils, sediments, composts and plant materials were analyzed for this study (Table II). All of the soil and sediment samples were dried at 110°C and ground using a mechanical mill. Plant materials were dried at 40°C and ground in a cross beater mill (Culatti AG, Zürich, Schwitzerland). This procedure yields particles that pass a 120 μm screen. Samples were weight to the nearest 0.001 mg using a Mettler-Toledo AT21 microbalance (Mettler-Toledo, Greifensee, Schwitzerland).

The significance of differences between a measured value and the reference value was tested by a one sample t-test at the 95% level of confidence. Differences between means obtained using the different methods were tested using both the F-test and the t-test for independent samples. Linear least square regression analysis was used to compare averages found with the two methods. For all statistical testing SPSS version 10 (SPSS Inc., Chicago, IL) was used.

RESULTS AND DISCUSSION

Results are presented in Table I for the quality control materials and in Table II for the samples. All materials were analyzed both with the automated dry combustion technique (dry combustion) and with the method of ashing followed by ion chromatographic detection of sulfate (ion chromatography). For all the reference materials, reference values, bias and recovery are also provided. The bias is calculated as the difference between the average of the measurements and the reference value, and the recovery as the percentage of the reference value recovered during the analysis.

TABLE I Total sulfur data of quality control materials[a]

Reference material	Analytical determination											
Type	*Dry combustion*							*Ion chromatography*				
	μ (%)	s_r *(%)*	$\bar{x} \pm$ CI (%)	*n*	s_r *(%)*	Δ	*Rec. (%)*	$\bar{x} \pm$ CI (%)	*n*	s_r *(%)*	Δ	*Rec. (%)*
Certified reference materials												
Beech leaves[b]	0.263 ± 0.008	4.92	0.257 ± 0.017	5	5.24	−0.006	97.77	0.245 ± 0.017	5	5.70	−0.018	93.22
Spruce needles[b]	0.170 ± 0.008	7.78	0.181 ± 0.011	6	5.94	+ 0.011	106.67	0.158 ± 0.030	4	11.8	−0.012	93.19
Confirmation materials												
Sulfanilamide[c]	18.62		19.04 ± 1.19	5	5.01	+ 0.42	102.27	16.29 ± 3.30	4	12.7	−2.33	87.47
Sodium sulphate[c]	22.57		23.15 ± 0.91	3	1.58	+ 0.58	102.55	22.52 ± 0.32	3	0.58	− 0.054	99.78

a. μ: True value; s_r – Relative standard deviation; $\bar{x}$ – Average; CI – Confidence interval at 95 %; n – Number of determinations; Δ – Bias; Rec. – Recovery.
b. Origin: BCR – standard reference material (Standard Measurements and testing Programme, Brussels).
c. Pure chemical compounds, supplied by CE Instruments, Milano, Italy (Sulfanilamide) and by Merck, Darmstadt, Germany (Sodium sulphate).

TABLE II Total sulfur data of soils and plants[a]

Sample	*Analytical determination*					
Type	*Dry combustion*			*Ion chromatography*		
	$\bar{x} \pm$ CI (%)	*n*	s_r (%)	$\bar{x} \pm$ CI (%)	*n*	s_r (%)
Soils						
River Meuse (Kotem, Belgium)	0.0524 ± 0.0097	6	17.6	0.0723 ± 0.0081	4	7.08
River Meuse (Vucht, Belgum)	0.0277 ± 0.0043	6	15.0	0.0321 ± 0.0064	5	16.0
Compost (IPALLE, Belgium)	0.2320 ± 0.0313	6	12.9	0.2136 ± 0.0155	5	5.85
Loam Clay (Gent, Belgium)	0.0267 ± 0.0035	5	10.6	0.0289 ± 0.0107	4	23.3
Tropical soil (Nkolbisson, Cameroon)	0.0172 ± 0.0022	5	10.2	0.0145 ± 0.0028	4	12.1
Tropical soil (Gao, Mali) **Plants**	0.0057 ± 0.0017	6	28.1	0.0051 ± 0.0007	4	8.06
Spruce needles (Gent, Belgium)	0.1371 ± 0.0122	6	8.47	0.1403 ± 0.0388	4	17.4
Ash-tree leaves (Gent, Belgium)	0.2332 ± 0.0058	5	1.99	0.2241 ± 0.0392	4	11.0
Oak leaves (Gent, Belgium)	0.2009 ± 0.0062	6	2.95	0.1716 ± 0.0294	4	10.8
Barley straw (Basilicata University, Italy)	0.2772 ± 0.0100	5	2.91	0.2750 ± 0.0197	4	4.50
Wheat flour (Central Laboratory, ARC, Finland)	0.1496 ± 0.0051	5	2.73	0.1227 ± 0.0577	5	18.9
Potato powder (Central Laboratory, ARC, Finland)	0.1631 ± 0.0166	5	8.20	0.1480 ± 0.0217	4	9.23

a. $\bar{x}$ – average; CI – Confidence interval at 95 %; n – Number of determinations; s_r – Relative standard deviation

Quality control

For the quality control materials, dry combustion yielded slightly higher values than the ion chromatography method (Table I). This is also reflected in the bias, i.e., the deviation from the reference value, which is generally positive for the dry combustion method and negative for the ion chromatography method. These findings are consistent with previously published data with respect to overall accuracy, precision and recoveries for similar quality control materials[2,4,5]. They warrant the use of ion chromatography in this study to compare with the dry combustion technique.

The results obtained for the reference materials with the two methods were not significantly different from the reference value (one sample t test at $p = 0.05$). Recoveries were good and slightly, though not significantly, lower for the ion chromatography method. On the other hand, reproducibility was better for the dry combustion method.

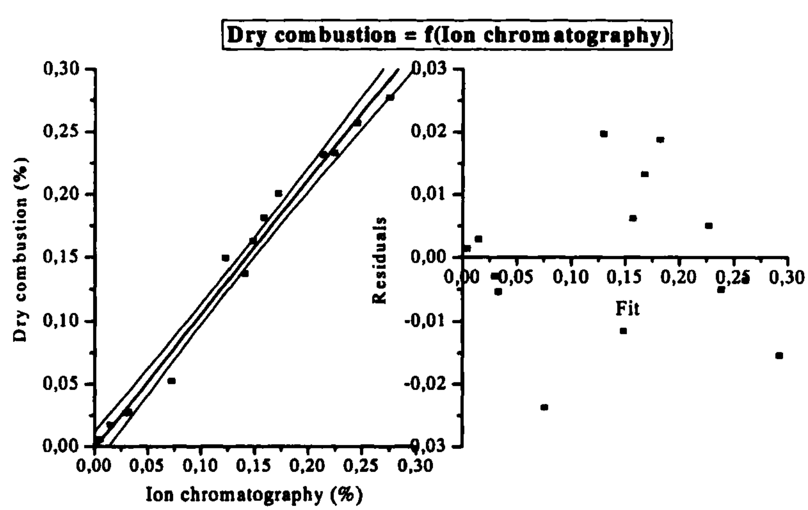
Total sulfur determination

Linear regression between averages obtained using the dry combustion method and these obtained using the ion chromatography method illustrates the very good agreement between the methods (Figure 1). The slope was not significantly different from unity ($p = 0.05$) and therefore indicates a perfect agreement between both methods within the random error. The intercept was not significantly different from zero, indicating the absence of any systematic deviation between the two groups of results.

After verification of normality and the existence of possible outliers, total sulfur data were compared with adequate two sample tests, the F test and the t test for independent samples. Differences were not significant with the exception of oak leaves and wheat flour (Table II).

For soils, characterized by low sulfur contents in the range of 0.01–0.05%, the precision of the results obtained by the two methods was similar. For plants and certified reference materials that had about five to tenfold higher sulfur contents, variances of the dry combustion method were in the range of these obtained for soils (Table II). For the method involving ion chromatography, variances increased with increasing total contents. The dry combustion method thus performed better with respect to reproducibility than the method involving ion chromatography.

The detection limit was evaluated as 3.3 times the standard deviation of residuals. For the dry combustion method, the detection limit for total sulfur in soils was estimated to be 0.0042 % based on a maximum sample size of 50 mg. This is



Y = A + B * X:

Parameter	Value	C.I.	R	R-Square(COD)	N
A	-0.00120	0.0136	0.9918	0.9836	14
B	1.068	0.0860			

FIGURE 1 Linear least squares regression between means for the different samples obtained by dry combustion and ion chromatography

below the manufacturer's specification of 0.01 %. For plants, assuming a maximum sample size of 6 mg, 0.04 % was found to be a practical detection limit. This is four times higher than the manufacturer's specifications but still lower than quantities usually found in this kind of samples. The detection limit evaluated for ion chromatography and for a maximum sample size of 50 mg was 0.0065 %, which is also sufficiently low to be of no concern.

CONCLUSIONS

Results obtained using the dry combustion method agreed closely with the method of ashing/ ion chromatography. At the same time, better precision, accuracy and recovery, particularly for the higher sulfur contents found in the plant samples, were achieved with the dry combustion method. Comparison with data obtained using an earlier version of the same equipment[3] clearly revealed that precision, accuracy and recovery of total sulfur analysis have improved significantly with currently available equipment.

The results presented indicate that the dry combustion technique has developed into an adequate method for the determination of low total sulfur contents in soils and plants.

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