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Analytical Controlled Losses of Potassium from Straw Ashes

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Accurate knowledge of the concentrations of potassium and other elements is critical for evaluating the effects of straw and other high-fouling biomass fuels in combustion boilers and other thermal systems. Development of accurate and precise analytical procedures is therefore essential for utilization of biomass fuels in energy production and high-temperature applications. By comparing the results of X-ray fluorescence (XRF) analyses with similar analyses done using instrumental neutron activation (INA), it is observed that 20–25% of the original K₂O content of straw ashes and slag can be lost during sample preparation for analyses. The loss occurs during heating of the ashes to determine loss on ignition probably as a result of the breakdown of sylvite (KCl). This loss can be significantly reduced, but not completely eliminated, if the analyses are performed on ashes that have not previously been heat-treated. The study poses the cautionary note that similar losses may occur during XRF analyses of other agricultural and soil samples containing high amounts of alkali halogens.

Introduction

Accurate information on the concentrations of potentially volatile elements such as potassium and chlorine in biomass ash is critical for predicting fouling potential and formulating mitigation strategies for biomass-fueled boilers and furnaces. Such information is likewise critical for utilization and disposal of ash residues and environmental monitoring and protection. In this paper we evaluate loss of potassium from wood, wheat straw, and rice straw ashes during sample preparation for standard X-ray fluorescence analyses (XRF). XRF analytical procedures include heating the sample prior to analysis. This study compares the XRF analytical results for major and minor elements for heated and unheated samples with similar results for potassium obtained by nondestructive instrumental neutron activation (INA) analyses. It is demonstrated that the amount of potassium loss is dependent on preparation methods and that modifications of standard laboratory procedures can significantly reduce such losses. The findings are likely of interest also to the analysis of other agricultural and soil samples containing high amounts of potassium.

Experimental Section

Fuel Selection and Ash Preparation. The selected fuels for the study are two common biomass materials in California. The first fuel is a straw from a medium-grain Japonica (variety M202) rice grown in Colusa County, CA. The second fuel is a wheat straw from Yolo County, CA. Additional data were obtained on a mixed conifer (white fir and ponderosa pine) whole-tree wood fuel obtained from a single fuel truckload at Wheelabrator-Shasta Energy Co., Inc., Anderson, CA. The fuels and the ashing procedures for this study are similar to those used in related studies on ashing and slag formation.^{1,2}

The fuels were dried and milled to a maximum 1/8 in. (3 mm) particle size. The final moisture content for the air-dried samples determined after oven-drying at 105 °C were 7.5% for rice straw, 7.8% for wheat straw, and 10.4% for wood (wet basis). The air-dried fuels were ashed in air in a large-volume, electric muffle furnace (Fisher Isotemp model 497). The temperature was ramped at 20 °C/min to 100 °C and then at 2 °C/min to a maximum of 525 °C. The temperature was dwelled at 400 °C for 3 h and again at 525 °C for 4 h. The furnace temperature was then dropped from the maximum 525 °C at 8 °C/min until 30 °C. The rice and wheat straw samples were ashed in open ceramic containers. The wood sample was ashed in a semi-closed, steel container with an airflow of 4.5 L/min admitted to the container when the temperature reached its maximum value. These ashing procedures allowed relatively large ash volumes to be produced under controlled temperatures without ignition. The low ash content of the wood required a large mass of wood in the furnace, hence the need

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Table 1. Ultimate Analyses of Fuels (% wet basis)^a

	wood	rice straw	wheat straw
carbon	48.54	38.50	43.81
hydrogen	5.22	3.56	5.10
nitrogen	0.07	0.55	0.58
sulfur	0.02	0.06	0.12
oxygen	36.55	36.30	35.27
chlorine	0.03	0.58	0.34
moisture (% wet basis)	10.4	7.5	7.8
ash (% dry basis)	1.2	22.1	9.8

^a Ultimate analyses by Hazen Research Inc., Golden, CO. Moisture and ash contents as determined at UCD.

to specifically limit the amount of air during ashing to avoid uncontrolled burning. The ash contents on a dry basis are 1.2% for the wood fuel, 22.1% for the rice straw, and 9.8% for the wheat straw. The ultimate elemental compositions (Table 1) were determined following the analytical recommendations of Miles et al.³ These ash powders were then subjected to further heating to determine compositional changes up to the melting point.

Experimental Heating Procedures. For each experiment about 20 g of the original ash powder prepared at 525 °C was pressed into a pellet (25 mm diameter). Individual pellets were placed in a bottom-loading Kanthal furnace (EPD high-temperature melting furnace) at a temperature between the original ashing temperature of 525 °C and the respective melting temperature of the ash. Experimental temperature intervals were about 50 °C for straws and 100 °C for wood. The range of temperatures investigated extended from 525 to 1525 °C for wood, to 962 °C for wheat straw, and to 1325 °C for rice straw. The experimental duration was 2 h for straw ashes and 3 h for wood ash. Pellets were placed on Pt foil to avoid reaction with the bottom alumina plate. The resulting experimental products were all powdered in an agate mortar or if required (due to clinkering) using a SPEX wolfram carbide mill. Further experimental details are provided elsewhere.² The experimental temperatures are given in Table 2.

Analytical Techniques. The major and minor oxide compositions of the products were determined by X-ray fluorescence on samples either unheated or heated for 3 h in air at 950 °C to determine loss on ignition (LOI), irrespective of their previous thermal history including temperatures above 950 °C. In addition, potassium and chlorine contents were determined by instrumental neutron activation. Detailed analytical conditions and procedures are given elsewhere,² and only a brief summary is given here. Samples treated at 950 °C for LOI determination are hereafter referred to as heated samples. Samples that were not heated to 950 °C are referred to as unheated samples.

X-ray Fluorescence. The analytical procedures closely followed guidelines commonly used in XRF laboratories.^{4,5,7} Loss on ignition (LOI) was determined by heating the ash powders in a muffle furnace at 950 °C for 3 h. The LOI is not corrected for iron oxidation. This is reasonable since the ashes were produced in air and the Fe₂O₃ content is low. All XRF analyses were conducted on fused glasses prepared from the ignited ash powders by mixing 0.75 g of sample with 3.75 g of a lithium borate flux. Fused glasses of the unheated ash were prepared in a similar way, except that the mixing proportions were calculated as 0.75(1 + LOI/100) g of sample, where LOI is the sample specific loss on ignition at 950 °C, and 3.75 g of

flux to yield a constant flux/sample ratio. The crucibles containing the mixtures were transferred to a muffle furnace and melted repeatedly at 1150 °C for 5 min with swirling of the crucible after 5 min. After fusion, the melt was quenched to a flat glass tablet. This procedure assumes that the LOI at 950 °C is identical to that at 1150 °C. The XRF major element analyses were performed on a PW2400 X-ray spectrometer using silicate rock reference materials for the calibrations.⁶ Typical analytical uncertainties based on counting statistics for wood and straws are given in Table 2.

Instrumental Neutron Activation. The INA technique is nondestructive and did not require heating or other treatments to the ash powders. From 20 to 120 mg of ash powder was sealed in a polyethylene vial. Vials, including a standard and reference materials, were irradiated in a TRIGA-type nuclear reactor at 1.8 MW power for 10 or 30 s. Assay of delayed gamma ray was performed using a Genie-VMS spectroscopy system from Canberra Industries with high-purity germanium detectors. Precision of analysis was better than 1.2% and 0.2% for K and Cl, respectively. The accuracy estimated from the results of the reference material was better than 3.7% and 6.0% for K and Cl, respectively.

Results

The compositions of the wood, wheat straw, and rice straw experimental products are listed as wt % oxides for the unheated ashes in Table 2 and for the heated (950 °C) ashes in Table 3. The INA results on the unheated ashes are included in Table 2.

The concentrations of K₂O determined by INA are systematically higher than the corresponding concentrations for both the heated and the unheated ashes determined by XRF (Figure 1). Using the INA analyses we can estimate the original concentrations of K₂O and thereby the loss of K₂O during preparation of the glass tablets at 1150 °C. The K₂O concentrations determined using XRF for the unheated powders deviate slightly from the INA concentrations (K₂O* in Table 2, linear regression in Figure 1 is K₂O* = 1.0849 × K₂O^{XRF} - 0.3429). This suggests losses during flux melting of 4.9–5.4% for rice straw ash and 6–6.3% for wheat straw ash (compare columns K₂O and K₂O* in Table 2), well outside the analytical uncertainty. The K₂O concentrations determined using XRF for the heated ashes in contrast strongly deviate from the INA concentrations (K₂O* in Table 3; linear regression in Figure 1 is K₂O* = 1.4141 × K₂O^{XRF} - 1.3782). This suggests losses amounting to 20% for rice straw ash and 25% for wheat straw ash during preparation of the ashes for XRF analyses (compare K₂O* columns in Tables 2 and 3).

Discussion

Standard XRF analytical procedures often involve determination of the total volatile components. This is normally done by measuring the weight loss (or loss on ignition) by heating the sample powder in air at 950 °C for 3 h or at similar conditions. This heated powder is to preserve scarce material utilized for preparing a glass tablet on which the XRF analysis is performed. The tablet is made by melting a mixture of powder and lithium borate flux at 1150 °C (cf. 7). The melting may be done repeatedly to ensure that the sample is completely melted. The preparation of glass tablets for XRF analyses thus often involves two heating/melting steps that both have potential for volatilizing potassium and

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Table 2. XRF Analyses of Unheated Ash (wt % oxides)^a

ID	T (°C)	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	K ₂ O*	K ₂ O** (INA)	P ₂ O ₅	volatiles (950 °C)	Cl (INA)	sum (-O=Cl)
wood																
WO-8	1525	12.76	0.15	6.87	1.48	2.27	7.35	45.55	0.35	6.96	7.21		4.38	9.33		97.44
WO-10	1425	13.42	0.16	4.54	1.63	2.55	7.68	48.84	0.40	6.59	6.81	7.53	4.87	6.39	<0.067	97.08
WO-7	1325	13.23	0.16	4.36	1.56	2.45	7.35	46.82	0.46	7.40	7.68		4.68	8.24		96.70
WO-9	1225	12.00	0.16	4.13	1.47	2.36	6.87	44.40	0.49	11.44	12.07		4.42	8.74		96.46
WO-6	1125	12.06	0.15	3.90	1.39	2.22	6.44	41.27	0.50	12.78	13.52	11.74	4.11	11.42	<0.067	96.24
WO-1	1011	12.35	0.15	3.66	1.37	2.08	6.05	39.25	0.49	12.97	13.73		3.92	13.67		95.97
WO-5	913	11.69	0.15	3.79	1.35	2.10	6.07	39.47	0.50	13.70	14.52		3.92	13.33		96.08
WO-4	816	11.72	0.13	3.71	1.32	2.09	6.03	39.03	0.49	13.34	14.13	13.62	3.85	13.94	<0.104	95.66
WO-3	718	10.14	0.12	3.25	1.19	1.87	5.33	34.50	0.43	11.74	12.39		3.38	22.94		94.89
WO-2	621	9.46	0.12	3.06	1.12	1.77	5.04	32.49	0.39	10.89	11.47		3.18	26.73		94.26
WO-S	525	9.35	0.13	3.12	1.14	1.76	4.93	32.06	0.39	10.72	11.29	12.29	3.13	27.59	<0.065	94.31
wheat straw																
WH-5	962	66.91	0.06	0.94	0.46	0.07	2.15	3.17	0.98	17.71	18.87	18.79	1.18	4.75	2.80	99.91
WH-4	913	66.35	0.05	0.89	0.42	0.07	2.12	3.12	0.91	18.00	19.19	19.91	1.16	5.27	3.32	100.20
WH-6	864	66.76	0.06	0.97	0.48	0.07	2.09	3.11	0.93	18.05	19.24	19.71	1.13	5.25	3.69	100.91
WH-3	816	65.45	0.05	0.91	0.44	0.08	2.10	3.12	0.92	18.85	20.11	20.49	1.17	4.92	3.86	100.14
WH-7	767	66.20	0.05	0.90	0.44	0.07	2.05	3.10	0.90	18.53	19.76	20.16	1.12	3.51	4.12	99.13
WH-2	718	64.72	0.05	0.80	0.39	0.07	2.06	3.06	0.89	19.32	20.61	20.09	1.14	3.32	4.27	98.17
WH-8	670	65.23	0.06	0.92	0.44	0.07	2.03	3.00	0.89	18.38	19.60	19.34	1.08	4.17	4.24	98.60
WH-1	621	62.88	0.05	0.77	0.34	0.07	1.98	2.97	0.87	18.57	19.80	19.37	1.10	6.94	4.12	98.79
WH-9	572	63.69	0.06	0.94	0.43	0.07	1.94	2.88	0.85	17.36	18.49	18.65	1.02	7.26	3.99	98.70
WH-S	525	57.47	0.05	0.77	0.39	0.07	1.82	2.80	0.80	16.55	17.61	17.41	1.05	14.91	3.58	98.65
rice straw																
R-13	1325	83.12	0.03	0.13	0.09	0.39	2.01	2.34	0.16	10.06	10.57	9.90	0.49	0.59	0.35	99.66
R-12	1225	79.94	0.02	0.12	0.09	0.39	2.00	2.34	0.17	10.16	10.67	9.69	0.64	0.28	<0.023	96.13
R-11	1125	82.94	0.03	0.14	0.09	0.39	2.02	2.34	0.17	10.13	10.64	10.39	0.68	0.71	<0.026%	99.65
R-10	1011	79.90	0.01	0.12	0.12	0.37	1.93	2.21	0.21	11.35	11.97	12.13	0.67	2.85	1.71	101.07
R-5	962	78.84	0.02	0.13	0.11	0.36	1.90	2.15	0.21	11.81	12.47	12.50	0.65	3.98	2.27	101.93
R-4	913	77.77	0.01	0.12	0.10	0.36	1.88	2.14	0.21	12.19	12.88	13.01	0.65	4.65	2.81	102.25
R-6	864	77.59	0.01	0.12	0.10	0.35	1.86	2.11	0.19	12.37	13.08	12.68	0.65	4.82	2.89	102.42
R-3	816	76.90	0.02	0.11	0.09	0.35	1.84	2.11	0.19	12.48	13.20	14.14	0.64	5.35	3.17	102.53
R-7	767	76.54	0.01	0.12	0.09	0.35	1.85	2.11	0.19	12.60	13.33	13.48	0.64	5.85	3.20	102.82
R-2	718	76.04	0.01	0.12	0.09	0.35	1.84	2.10	0.18	12.47	13.19	13.80	0.63	6.59	3.39	103.05
R-8	670	75.33	0.01	0.11	0.09	0.34	1.82	2.06	0.18	12.54	13.26	13.06	0.63	7.18	3.25	102.81
R-1	621	75.16	0.01	0.11	0.08	0.34	1.81	2.05	0.18	12.49	13.21	13.41	0.63	7.18	3.45	102.73
R-9	572	74.47	0.01	0.11	0.09	0.35	1.82	2.05	0.18	12.28	12.98	12.69	0.62	7.95	3.21	102.43
R-S	525	72.55	0.01	0.11	0.08	0.34	1.74	2.00	0.16	11.33	11.95	12.47	0.60	10.94	3.18	102.33
uncertainty (counting statistics)																
wood ash		0.09	0.01	0.07	0.05	0.01	0.08	0.18	0.03	0.05			0.04			
straw ash		0.23	0.01	0.03	0.03	0.01	0.04	0.05	0.04	0.07		0.16	0.02		0.06	

^a Vol. (950 °C) is the loss on ignition at 950 °C. Cl (INA) is chlorine as determined on unheated ashes by neutron activation analyses. K₂O* (1150 °C) is the K₂O content corrected for the effect of fusion at 1150 °C (K₂O* = 1.0849 × K₂O - 0.3429, see text). K₂O** is the K₂O content determined by neutron activation analyses on ashes unheated and unmelted. Sum (-O=Cl) is the total corrected for oxygen equivalent of chlorine.

chloride, among other elements, and thus reducing the concentrations of these elements. The loss on ignition determined at 950 °C is corrected for the effect of oxidation (Fe), and the remaining loss is assumed to constitute the sum of the common volatiles (C, H, S, and N) expressed as oxides and other partially volatile components (K, Na, Cl). The final analysis is typically presented as in Table 3, including a volatile component that together with the major and minor elements ideally sum to 100%, provided that all elements were analyzed and furthermore analyzed accurately. Determination of volatile components may be nonessential for some applications and consequently can be eliminated for routine XRF analyses.⁸ In this case, the result is presented as oxides normalized to 100% and with all Fe as Fe₂O₃. An accurate knowledge of volatile components (H, C, S, N, K, Cl) is, however, essential for understanding combustion processes, and knowledge of LOI is the minimum requirement for proper interpretation of analyses of biomass ashes and slag.

Loss of K₂O as a result of heating from biomass samples are well documented.^{1,2,9,10} The loss commences at about 750 °C for typical straw ashes and appears to be related to the breakdown of sylvite.² The observed loss of K₂O from heating straw ashes to 950 °C for the determination of LOI as well as fusing at 1150 °C are therefore expected. The present results show that performing the XRF analyses on unheated powder can significantly reduce the loss.

Ashing studies² have shown that the weight loss continues to increase to 1200 °C, suggesting that volatile components (including K and possibly Cl) are present to temperatures well above 950 °C. The LOI for the wheat straw ash at 950 °C varies between 5% (962 °C ash) and 15% (525 °C) (Table 2). For rice straw the values range from 0.6% (1325 °C) to 11% (525 °C), and for the wood ash values range from 9% (1525 °C) to 28% (525 °C). Thus, the 950 °C ashes still contain significant amounts of volatile components (wheat straw 5%, rice

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Table 3. XRF Analyses of Ash Heated to 950 °C (wt % oxides)^a

ID	T (°C)	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	K ₂ O*	P ₂ O ₅	vol. (950 °C)	sum
wood														
WO-8	1525	12.90	0.15	4.28	1.51	2.36	7.73	47.82	0.53	5.51	6.41	4.50	9.33	96.62
WO-10	1425	13.82	0.17	4.66	1.63	2.58	7.83	49.71	0.52	5.09	5.82	4.95	6.39	97.35
WO-7	1325	13.56	0.17	4.48	1.59	2.47	7.48	48.04	0.60	5.65	6.61	4.74	8.24	97.02
WO-9	1225	12.19	0.16	4.23	1.52	2.42	7.03	45.52	0.61	9.19	11.62	4.51	8.74	96.12
WO-6	1125	12.36	0.15	3.95	1.46	2.26	6.54	42.33	0.64	11.00	14.18	4.21	11.42	96.32
WO-1	1011	12.65	0.16	3.99	1.46	2.15	6.20	40.30	0.72	10.93	14.08	4.00	13.67	96.23
WO-5	913	13.38	0.15	3.84	1.40	2.12	6.09	39.95	0.66	11.28	14.57	3.99	13.33	96.19
WO-4	816	14.42	0.15	3.81	1.34	2.07	6.04	39.41	0.68	10.97	14.13	3.87	13.94	96.70
WO-3	718	10.77	0.13	3.45	1.23	1.95	5.67	36.37	0.62	10.06	12.85	3.58	22.94	96.77
WO-2	621	10.05	0.12	3.28	1.19	1.85	5.44	34.77	0.58	9.41	11.93	3.42	26.73	96.84
WO-S	525	10.48	0.12	3.21	1.35	1.82	5.33	34.14	0.56	9.14	11.55	3.37	27.59	97.11
wheat straw														
WH-5	962	68.65	0.06	1.00	0.52	0.08	2.19	3.27	1.13	14.98	19.81	1.19	4.75	97.82
WH-4	913	68.47	0.05	0.94	0.47	0.08	2.17	3.26	1.11	14.84	19.61	1.17	5.27	97.83
WH-6	864	68.50	0.06	1.05	0.51	0.08	2.14	3.20	1.15	14.61	19.28	1.12	5.25	97.67
WH-3	816	67.56	0.06	0.97	0.49	0.08	2.16	3.22	1.28	15.44	20.46	1.17	4.92	97.35
WH-7	767	68.28	0.06	0.97	0.48	0.08	2.12	3.19	1.29	15.63	20.72	1.12	3.51	96.73
WH-2	718	66.84	0.05	0.84	0.44	0.08	2.11	3.21	1.36	16.58	22.07	1.16	3.32	95.99
WH-8	670	68.00	0.06	0.98	0.50	0.08	2.10	3.20	1.35	15.23	20.16	1.10	4.17	96.77
WH-1	621	65.55	0.05	0.82	0.41	0.07	2.07	3.11	1.26	15.41	20.41	1.12	6.94	96.81
WH-9	572	65.89	0.06	0.96	0.50	0.07	2.00	3.04	1.27	14.57	19.23	1.05	7.26	96.67
WH-S	525	60.25	0.05	0.80	0.43	0.07	1.91	2.92	1.30	13.49	17.70	1.09	14.91	97.22
rice straw														
R-13	1325	84.44	0.01	0.32	0.12	0.39	2.02	2.35	0.51	8.58	10.75	0.49	0.59	99.82
R-12	1225	84.30	0.02	0.31	0.12	0.39	2.02	2.36	0.52	8.84	11.12	0.65	0.28	99.81
R-11	1125	83.56	0.01	0.17	0.11	0.39	2.02	2.35	0.44	9.15	11.56	0.68	0.71	99.59
R-10	1011	80.69	0.02	0.12	0.13	0.37	1.95	2.24	0.54	9.01	11.36	0.67	2.85	98.59
R-5	962	79.78	0.02	0.13	0.12	0.37	1.93	2.21	0.55	8.93	11.25	0.66	3.98	98.68
R-4	913	78.93	0.02	0.13	0.10	0.37	1.91	2.20	0.57	8.89	11.19	0.66	4.65	98.43
R-6	864	78.70	0.02	0.12	0.10	0.37	1.90	2.20	0.57	9.01	11.36	0.65	4.82	98.46
R-3	816	78.35	0.02	0.13	0.10	0.36	1.89	2.19	0.54	8.88	11.18	0.65	5.35	98.46
R-7	767	77.73	0.02	0.12	0.11	0.37	1.88	2.16	0.53	9.01	11.36	0.65	5.85	98.43
R-2	718	77.28	0.02	0.13	0.10	0.36	1.85	2.16	0.54	8.94	11.26	0.64	6.59	98.61
R-8	670	76.67	0.02	0.11	0.09	0.36	1.84	2.12	0.56	8.89	11.19	0.64	7.18	98.48
R-1	621	76.31	0.02	0.12	0.10	0.35	1.82	2.09	0.51	9.20	11.63	0.63	7.18	98.33
R-9	572	75.51	0.02	0.12	0.10	0.35	1.82	2.13	0.54	9.01	11.36	0.64	7.95	98.19
R-S	525	73.30	0.02	0.11	0.10	0.34	1.76	2.02	0.52	8.57	10.74	0.61	10.94	98.29

^a Vol. (950 °C) is the loss on ignition at 950 °C. K₂O* is the K₂O content corrected for the effect of heating at 950 °C and fusion at 1150 °C (K₂O* = 1.4141 × K₂O - 1.3782, see text).

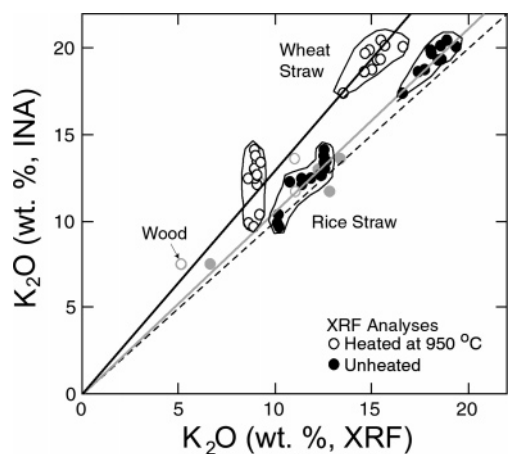


Figure 1. K₂O content of ashes determined by XRF and INA. Solid symbols are unheated ashes, while open symbols are ashes heated at 950 °C. See text for discussion and linear regression equations.

straw 4%, and wood ash 13%) that potentially may be lost during the 1150 °C flux melting.

Thermodynamic modeling using the FactSage database¹¹ suggests that a sodium sulfate melt for rice straw and wheat straw ash may be stable to temperatures of

1100–1200 °C after which it decomposes. Analyses of the straw ashes suggest that 0.7–1.7% SO₂ is present (Table 4) and supports the presence of below 5% sulfate in the melting ashes. Analyses suggest that the CO₂ content is low and negligible for the straw ashes, but its concentration evidently depends on the efficiency of the ashing process. Chlorine is present in the straw ashes as sylvite that is stable to between 1000 and 1125 °C.² It is thus reasonable to suggest that the continued weight loss during heating above 950 °C can be attributed to the decomposition of sulfates and sylvite and loss of SO₂, K₂O, and Cl. However, there is no compelling evidence to suggest that CO₂ is present in a large amount in the straw ashes heated to 950 °C.

The wood ash contains high amounts of carbonate seen as CO₂ in Table 4. Thermodynamic modeling predicts that calcite completely decomposes at 900–1000 °C. Calcite was detected in the ashes only to about 700 °C.² It is possible that above this temperature calcite is present in low concentrations, undetected by the X-ray diffraction techniques, due to incomplete equilibration of the ash or slag samples. The SO₂ and Cl contents of the wood ash are low and cannot explain the weight loss at high temperature. This leaves decomposition of carbonate and the loss of K₂O as the main reasons for the prolonged weight loss well after most volatile components are driven off from heating. Loss

(11) Bale, C. W.; Chartrand, P.; Degterow, S. A.; Eriksson, G.; Hack, K.; Ben Mahfoud, R.; Malancon, J.; Pelton, A. D.; Petersen, S. *Calphad* 2002, 26, 189–228.

Table 4. Summary of Compositions of 525 °C Ashes (wt % oxides)^a

	wheat straw					rice straw					wood				
	unheated		heated			unheated		heated			unheated		heated		
SiO ₂	57.47	69.38	60.25	73.83	69.64	72.55	81.03	73.30	83.92	80.63	9.35	13.89	10.48	15.07	14.45
TiO ₂	0.05	0.06	0.05	0.06	0.06	0.01	0.01	0.02	0.02	0.02	0.13	0.19	0.12	0.17	0.17
Al ₂ O ₃	0.77	0.93	0.80	0.98	0.93	0.11	0.12	0.11	0.13	0.12	3.12	4.64	3.21	4.62	4.42
Fe ₂ O ₃	0.39	0.47	0.43	0.53	0.49	0.08	0.09	0.10	0.11	0.11	1.14	1.69	1.35	1.94	1.86
MnO	0.07	0.08	0.07	0.09	0.08	0.34	0.38	0.34	0.39	0.37	1.76	2.62	1.82	2.62	2.51
MgO	1.82	2.20	1.21	1.48	1.40	1.74	1.94	1.76	2.01	1.94	4.93	7.33	5.33	7.67	7.35
CaO	2.80	3.38	2.92	3.58	3.38	2.00	2.23	2.02	2.31	2.22	32.06	47.64	34.14	49.11	47.06
Na ₂ O	0.80	0.97	1.30	1.59	1.50	0.16	0.18	0.52	0.60	0.57	0.39	0.58	0.56	0.81	0.77
K ₂ O	17.61	21.26	13.49	16.53	21.26	11.95	13.35	8.57	9.81	13.35	11.29	16.78	9.14	13.15	16.78
P ₂ O ₅	1.05	1.27	1.09	1.34	1.26	0.60	0.67	0.61	0.70	0.67	3.13	4.65	3.37	4.85	4.65
L.O.I.	14.91		14.91			10.94		10.94			27.59		27.59		
Cl	3.58		3.58			3.18		3.18			<0.064		<0.064		
sum	101.32	100.00	100.10	100.00	100.00	103.66	100.00	101.47	100.00	100.00	94.89	100.00	97.11	100.00	100.00
sum (-O=Cl)	100.51		99.29			102.94		100.75			94.88		97.10		
SO ₂	1.66		1.66			0.67		0.67			0.69		0.69		
CO ₂	0.19		0.19			0.22		0.22			6.24		6.24		

^a The first column for each fuel ash type is the analysis done on the unheated ash (Table 2). The second column is similar to column 1 but calculated volatile-free to 100%. The third column is the analysis done on the heated ash (Table 3). The fourth column is similar to column 3 but calculated volatile-free to 100%. The fifth column is the analysis done on the heated sample recalculated assuming the estimated original K₂O content (Table 2). SO₂ and CO₂ contents were determined by Hazen Research, Inc., CO, on ashes produced at 600 °C.

of K₂O from wood ashes has been experimentally well documented^{9,10} and can be so severe that all K₂O is lost.

Semiquantitative XRF analyses of the 1150 °C glass tablets produced from the unheated ashes suggest that SO₂ and Cl are present in significant amounts for the wheat straw ash amounting to a total of up to 4%. This suggests that at least these components can partially be quenched into the flux glass without being released. The sum of the oxides adjusted for the oxygen equivalent of chlorine and assuming some SO₂ and small amounts of CO₂ does not suggest unanalyzed elements or components. In fact, the only detectable minor and trace elements that were not analyzed are Zn (wood only) and Sr. The concentrations of these elements, judging from XRF semiquantitative analyses, are too low to have a significant effect on the present discussion.

Table 4 shows the effect of adjusting the K₂O content of the heat-treated ashes to its original value and recalculates the remaining oxides to a total sum of 100%. These recalculated compositions are compared to the compositions of the unheated ashes (Table 4). It is seen that there is a close correspondence for most oxides, suggesting that the effect of heating was a simple enrichment due to loss of K₂O. The only notable exception is Na₂O, which for reasons not understood appears to be enriched during heating.

The partial retention of K₂O in the unheated powder during flux melting means that the LOI determined at 950 °C is not directly applicable to the 1150 °C flux melting. The heat-treated powder was mixed with flux in the proportions 0.75 g of sample and 3.75 g of flux. For the unheated ashes the mixing proportions of the sample and the flux were adjusted by the amount expected to be released during flux melting based on the LOI determined at 950 °C. If this value were actually lower due to the increased retention of K₂O (and other components such as Cl and S), the resultant glass may have been relatively enriched in sample material and the analyzed concentrations too high. It would, as seen for the straw ashes, consequently be expected that the sum of the components would be higher for the unheated than for the heated ashes (Table 4). For this reason we cannot accurately assess whether the slightly lower concentrations seen for the unheated ashes when compared to the INA analyses is due to real

losses during flux melting or the effect of using an incorrect dilution factor for sample-flux mixing.

The flux fusion technique was introduced to modern XRF analyses to eliminate mineralogical matrix effects and today widely used to determine major and minor oxide concentrations of silicate materials. An alternative and traditional method is to use pressed powder pellets that do not require destructive procedures during preparation. Powder pellets are still widely used for analyzing trace elements. However, for major elements powder pellets are subject to large matrix effects that can only be reduced by using regressed standard curves based on materials similar to the unknowns. Considering that few (if any) well-documented standards of comparable biomass materials exist, this option is not at present feasible.

An accurate knowledge of the LOI during flux fusion is essential for data reduction. The assumption that LOI determined by heating several hundred degrees below fusion temperatures also apply to fusion temperature cannot be substantiated. Thus, standard XRF analyses done on fused tablets made from unheated ashes are subject to volatile losses and thus an erroneous dilution factor.

Conclusions

The results of these analyses demonstrate that from 20% to 25% of the original K₂O content of straw ashes and slag can be lost during standard XRF analyses. The loss occurs during heating to determine loss on ignition likely as a result of the breakdown of sylvite. This loss can significantly be reduced, but not completely eliminated, if the analyses are performed on samples that have not previously been heat-treated. Large K₂O losses may also occur during analyses of other agricultural and soil samples containing high amounts of potassium. Development of accurate analytical procedures is essential for proper analyses of the ashes of common biomass materials. This includes preparation and documentation of biomass materials that can be used as standards.

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