THE SEARCH FOR AN ACCURATE AND PRACTICAL MEANS FOR TESTING RESIDUE FROM COMBUSTION OF MUNICIPAL SOLID WASTE FOR PERCENT COMBUSTIBLES AND ENERGY CONTENT

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ABSTRACT

When municipal solid waste combustors are tested for thermal performance, residue testing is usually required to establish the percentage of combustible material in the residue and/or the energy loss due to combustible material in the residue. The test methods traditionally used to test residue from combustion of coal for combustible content are adaptations of test methods developed for testing unburned coal or coke. These test methods do not lend themselves to testing residue from municipal solid waste because of the metal, glass, ceramics, stone and the like in residue that make preparation of an analysis sample complex. In addition, the solid residue from acid gas scrubbing which becomes a part of the residue may be subject to chemical reaction during testing that will skew the results. The American Society of Mechanical Engineers, Performance Test Code Committee 34 on Waste Combustors with Energy Recovery has accepted the challenge to develop a test method to produce reliable results when residue from combustion of municipal solid waste is tested. This paper is a Progress Report on their findings.

INTRODUCTION

The ASME Performance Test Code Committee 34 on Waste Combustors with Energy Recovery is endeavoring to establish an accurate and practical means to measure percent combustibles in the residue and the unburned combustible loss for municipal solid waste combustors with energy recovery. Three approved Performance Test Codes [1] presently include procedures for measuring the unburned combustibles in residue and a proposed Code is being finalized that also requires measuring combustibles in residue.

(*1*) PTC 3.2-1990 Coal and Coke [issued February 1993]

(*2*) PTC 4.1-1979 Steam Generating Units

(*3*) PTC 33-1978 Large Incinerators

(*4*) PTC 4 Combustible Fuel Fired Steam Generators 1993 Industry Review Draft

The procedures prescribed in the Performance Test Codes rely on ASTM Standard Test Methods developed for testing unburned coal and coke. None of the ASTM test methods contain any indication that they are suitable for testing combustion residues.

ASTM Standard Test Methods [2]

The following are synopses of the laboratory test methods referenced in the Performance Test Codes.

D1756 Standard Test Method for Carbon Dioxide in Coal. The determination of carbon dioxide is made by decomposing with acid a weighed quantity of sample in a closed system and absorbing the carbon dioxide in an absorbent. The increase in weight of the absorbent is a measure of the carbon dioxide in the sample used. The

sample is material pulverized to pass a 250 micrometer (No. 60) sieve with a nominal sieve opening of 0.01 inch. Water and then hydrochloric acid are added to the sample. Decomposition takes place as the sample, water and acid are heated to a slow boil for 5 minutes. Note, this Test Method is to determine carbon dioxide in a coal sample; it does not reference or determine an adjustment to the carbon content of coal determined by D3178 or to the ash content of coal determined by D3174. (A similar test method has not been developed for refuse derived fuel.)

D3174 Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal. In this test method, ash is determined by weighing the residue remaining after burning coal or coke under rigidly controlled conditions of sample weight, temperature, time, atmosphere, and equipment specifications. The sample is material pulverized to pass a 250 micrometer (No. 60) sieve with a nominal sieve opening of 0.01 inch. The sample weight is approximately 1 gram. The ashing temperature is at 700 to 750 C for two hours. While this test method references D1756, no guidance is provided to adjust the ash percentage for the carbon dioxide determined by D1756. (A similar test devised for refuse derived fuel rather than coal or coke is *E830 Standard Test Method for Ash in the Analysis Sample of Refuse Derived Fuel* which prescribes ashing at 575 ±5°C.)

D3178 Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke. The determination of carbon and hydrogen is made by burning a weighed quantity of sample in a closed system and fixing the products of combustion in an absorption train after complete oxidation and purification from interfering substances. The combustion unit prescribed is a quartz or high silicon glass tube about 1 meter long with an internal diameter of about 20 millimeters fitted with three individually controlled, electronically heated, furnace sections. These test methods determine the total percentages of carbon and hydrogen in the coal as analyzed, and include any carbon in carbonates and the hydrogen in moisture or in the water of hydration of silicates. The sample is material pulverized to pass a 250 micrometer (No. 60) sieve with a nominal sieve opening of 0.01 inch. The sample weighs approximately 0.2 grams. In the course of the test, the sample is heated to 850 to 900 C. The sample is held at this temperature for about 30 minutes. Note, this test method does *not* reference D1756, or any other ASTM Standard, as the means for adjusting carbon percentage for carbonates in coal or coke. (A similar test devised for refuse derived fuel rather than coal or coke is *E777 Standard Test Method for Carbon and Hydrogen in the Analysis Sample of Refuse Derived Fuel.*) (D3178 and E777 are rarely, if ever, used today because of the 1 hour or more time requirement for each test. Instead, most laboratories use instruments developed to measure carbon and hydrogen without the elaborate absorption train required by these ASTM Standards.)

D3286 Standard Test Method for Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter. Calorific value of coal or coke samples is determined in this test method by burning a weighed sample, in oxygen, in a calibrated isoperibol bomb calorimeter under controlled conditions. (Isoperibol is a term meaning constant temperature jacket.) The calorimeter is standardized by burning benzoic acid. The sample is material pulverized to pass a 250-micrometer (No. 60) sieve with a nominal sieve opening of 0.01 inch. The sample weight for testing is 1 gram. *(D2015 Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter* is a similar test method for coal and coke utilizing an adiabatic bomb calorimeter where the jacket temperature is allowed to rise.) (A similar test devised for refuse derived fuel rather than coal or coke is *E711 Standard Test Method for Gross Calorific Value of Refuse Derived Fuel by the Bomb Calorimeter.) (None of these test methods provide guidelines for the use of a combustion aid.*)

D5373 Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke. These test methods are a general guideline for the use of proprietary instruments. These instruments convert the sample to carbon dioxide, water vapor, nitrogen oxides and ash for subsequent quantitative determination of the gases in an appropriate reference gas stream. These instruments measure thermal conductivity in millivolts. Once initiated, these instruments performed analyses and automatically print out results in less than five minutes. Sample size can range from 0.001 to 0.005 grams depending on the instrument manufacturer's recommendations. These instruments are marketed by Perkin-Elmer, LECO and perhaps others. The cost is in the $40,000–$50,000 range. The sample is material pulverized to pass a 75-micrometer (No. 200) sieve with a nominal sieve of 0.003 inch.

E955 Standard Test Method for Thermal Characteristics of Refuse Derived Fuel Macrosamples. A 2-pound sample of RDF is dried and ashed successively. The moisture, combustibles and non-combustibles content are determined gravimetrically. This test method was developed as a means of determining thermal characteristics of a large sample of RDF without extensive processing of laboratory samples. The heating value of the macrosample of RDF is calculated using an established moisture and non-combustible free heating value. Similarly, this test method provides for determining the heating value of residue from combustion of RDF using a pre-established moisture and ash free heating value

of the combustible material in the residue. If the moisture and ash free heating value is not established by testing, a heating value of 12,000 Btu/lb is suggested.

Test Concepts for Measuring Combustibles in Residue

In summary, three different concepts are prescribed by the referenced Performance Test Codes. These three concepts are:

1. *Bomb calorimetry* to measure heating value of residue.
2. *Elemental analysis* to measure carbon alone or carbon and hydrogen in the residue from which heating value of the residue is calculated.
3. *Loss on ignition* with the presumption that weight loss after adjustment for inorganic carbon, is carbon with a higher heating value of 14,500 Btus per pound from which heating value of the residue is calculated.

All three test concepts have vociferous adherents.

Concerns When Using These Concepts for Coal and Coke. When these three concepts are used to determine the unburned combustibles in the residue from combustion of coal or coke, concerns are raised:

1. *Bomb calorimetry.* Because the percent of combustibles in residue is a small percentage of the total residue, bomb calorimetry is only effective if a combustion aid (a combustible material with a known heating value such as benzoic acid or mineral oil) is mixed with the residue; and when the calorimeter results are known, the effect of the combustion aid is deducted. In other words, a relatively large amount of combustible material with a known heating value is added to a relatively small amount of combustible material in the residue with an unknown heating value, the bomb is fired and the heating value of the relatively large amount of combustible material is subtracted from the calorimeter measurement to determine the heating value of the small amount of combustible material. A small error in the heat content of the combustion aid can become a large error in the heat content of the residue.

2. *Elemental analysis.* While bomb calorimetry and loss on ignition ASTM procedures test a one gram sample, the ASTM glass tube device for elemental analysis tests a 0.2 gram sample; and the test instruments used in most fuel laboratories test 0.005 gram or less size samples. (To put sample size in perspective, once the residue sample has been dried, pulverized and made ready for analysis, a one gram sample will nearly fill a half teaspoon kitchen measure, a 0.2 gram sample will be about one-third of a quarter teaspoon kitchen measure, and a 0.005 gram sample will be the size of a pin head.) When elemental analysis tests are applied to residue from combustion of coal or coke, the representativeness of the sample analyzed is problematic.

3. *Loss on ignition.* The referenced loss on ignition procedure, which was developed to determine the ash content of coal or coke, prescribes heating the sample 700 to 750 C (1300–1380 F). At these temperatures, some components of ash are subject to chemical reactions that alter the results.

Additional Concerns for Municipal Solid Waste Combustors with Energy Recovery. When the three test concepts described above are applied to residue from municipal solid waste combustors with energy recovery, additional concerns arise. Major concerns are:

1. To the eye, ash residue from combustion of coal or coke appears to be reasonably homogenious; however, ash residue from combustion of municipal solid waste is obviously heterogeneous. With this obvious difference, the ability to obtain a representative 1 gram sample is more problematic than for coal and coke, and a representative 0.005 gram sample is exceedingly so.
2. All of the ASTM test methods referenced for the three concepts require grinding of the samples to pass a nominal sieve opening of 0.01 inch. Residue from combustion of municipal solid waste contains metals, glass, ceramics and other material that does not lend itself to grinding. Therefore, ungrindable materials must be hand picked from the sample and factored back into the test results once the remaining material is tested. This is a time consuming procedure and subject to error.
3. Combustible material remaining in residue from combustion of municipal solid waste inevitably contains some carbohydrates which have a heating value far less than the 14,500 Btus per pound used for carbon in the residue from coal or coke. The most prevalent carbohydrate, cellulose ($C_6H_{10}O_5$), has a heating value of less than 8,000 Btu/lb.
4. Most waste combustors with energy recovery designed to combust municipal solid waste now include acid gas scrubbers. Scrubbing is achieved by introducing a chemical sorbent into the gas stream to react with acid gases. Consequently, residue from combustion of municipal solid waste includes reaction products from acid gas scrubbers as well as unreacted sorbent. These materials are subject to chemical breakdown with heat. The loss of weight through chemical breakdown results in a falsely high measure of unburned combustibles in the residue unless adjusted or allowed for in some way.

PRELIMINARY INVESTIGATION BY PTC 34

Data from Recent Acceptance Tests

In 1992, comprehensive data became available from residue testing at a municipal waste combustor with energy recovery. During the Acceptance Test, residue samples were collected in increments each of eight days to form eight gross samples. Each day's gross sample was

mixed in a portable concrete mixer. A small shovel was used to scoop portions of each day's gross sample into three large freezer-type ziplock bags to form three laboratory samples. Each laboratory sample weighed about two pounds. Each of the ziplock bags containing laboratory samples was manipulated to remove as much air as possible before closing. Each bag was placed in another ziplock bag. One of the samples from each test day was sent to a laboratory for analysis. The other two samples were retained. When higher than expected levels of combustible material were reported in the residue, a dispute ensued which led to arbitration. During arbitration, a second sample for each of the test days was sent to a second laboratory for corroboration of the first laboratory's results. Results from the two laboratories were significantly different. Therefore, the third sample for seven of the eight test days was sent to a third laboratory for more comprehensive testing. Results reported by the third laboratory were markedly different from results from the other two laboratories. Relative results from the three laboratories are displayed on Table 1.

TABLE 1 DETERMINATION OF COMBUSTIBLES LEVEL IN COMBINED RESIDUE RELATED TO A BASE OF 1.00

	LABORATORY 1		LABORATORY 2			LABORATORY 3					
ASTM STD.	D3174 750 C	D1756 CO_2	D3174 550 C	D3174 750 C	D1756 CO_2	D3174 550 C	D3174 750 C	D1756 CO_2	D3178 C	D3178 C+H	D3286 HHV*
DAY 1	0.56	0.14	1.00	1.14	0.15	--	--	--	--	--	--
DAY 2	0.80	0.28	1.06	1.21	0.20	0.41	0.72	0.21	0.31	0.34	0.28
DAY 3	1.01	0.29	1.21	1.42	0.17	0.60	0.88	0.24	0.34	0.60	0.38
DAY 4	1.26	0.51	1.15	1.31	0.17	0.40	0.57	0.17	0.33	0.37	0.27
DAY 5	1.53	0.40	1.05	1.21	0.14	0.40	0.56	0.21	0.39	0.42	0.31
DAY 6	1.53	0.41	0.75	0.81	0.13	0.45	0.56	0.18	0.32	0.36	0.29
DAY 7	1.30	0.31	0.74	0.77	0.19	0.41	0.45	0.15	0.38	0.42	0.30
DAY 8	1.30	0.48	1.07	1.12	0.21	0.52	0.66	0.22	0.35	0.39	0.31
AVERAGE	1.16	0.35	**1.00**	1.12	0.17	0.46	0.63	0.20	0.35	0.40	0.31
RANGE, %	+30 -50	+45 -60	+20 -20	+25 -30	+25 -25	+30 -15	+40 -30	+20 -25	+10 -10	+25 -15	+25 -15

* Btu/lb converted to percent combustibles at 12,000 Btu/lb of combustibles per E955

The test protocol for this Acceptance Test specified a loss on ignition determination using D3174 except that the furnace temperature was to be 550 C rather than 700 to 750 C. The protocol called for adjusting the results for carbonates using D1756 to adjust for $CaCO_3$ in the scrubber residue. For reasons unknown, the first laboratory performed the loss on ignition test at 750 C rather than 550 C. Therefore, when the second laboratory was contracted to test the second set of samples, it established the weight loss using ASTM D3174 successively at 550 C and 750 C. Note on Table 1, for the second laboratory, that if the carbon dioxide measured by D1756 is deducted from the loss on ignition weight loss at 750 C on average, the adjusted weight loss would approximate the weight loss determined by loss on ignition at 550 C. This suggests that the carbon dioxide measured by D1756 is not driven off during loss on ignition at 550 C, but it is driven off between 550 C and 750 C. (The author has not been able to understand why a significant level of $CaCO_3$ should be in the scrubber residue, since the sorbent, $Ca(OH)_2$ reacts with HCl to form $CaCl_2$ and with SO_2 to form $CaSO_4$.)

The third laboratory was called on to repeat the loss on ignition test procedure that was run by the second laboratory, and in addition, measured carbon and hydrogen in the sample by means of D3178 and measured higher heating value by means of a bomb calorimeter using D3286. (The sample for Day 1 was not available for testing by the third laboratory.) Note the disparity in D3174 results on Table 1 between the second and third laboratory. Again however, the difference between loss on ignition at 550 C and 750 C on average corresponds to the carbon level measured by D1756. (If one wants to adjust the D3178 carbon or carbon plus hydrogen columns for carbonates determined by D1756, the carbon dioxide data should be multiplied by 0.273 to obtain the carbon in carbon dioxide.) The results for the bomb calorimeter were converted to sample weight loss using the precept of E955 that combustibles in residue have a heating value of about 12,000 Btu/lb moisture and ash free.

Because of the high level of combustibles in the residue during the Acceptance Test, the results displayed on Table 1 are not the actual percentage of combustibles in the residue sample; rather, they are all a ratio of an assumed base of 1.00 for the average loss on ignition established by the second laboratory using D3174 at 550 C (the first test results purported to follow the test protocol).

Also in 1992, data became available from a municipal waste combustor with energy recovery in New York State where the New York State Department of Environmental Conservation (DEC) specified a procedure for establishing the combustibles in residue using methods developed for water and wastewater. Briefly, these methods prescribe heating a sample to 105 C to drive off water, then the sample is to be heated to 550 C to drive off combustible material, and the difference in weight between the sample at 105 C and 550 C is to be counted as unburned combustible. The municipal waste combustor system supplier was concerned that bonded water in the unreacted slaked-lime sorbent in the residue would be driven off between 105 C and 180 C and the bonded water driven off would be counted as unburned combustible in the residue using the DEC method. The system supplier proposed to heat the sample to 180 C before heating it to 550 C so that the difference between the weight at 180 C and 550 C would more accurately represent the level of unburned combustible in the residue. The Engineer for the local solid waste authority agreed to this concept and approved a procedure to successively heat residue to 105 C, 180 C and then to 550 C. However, during the test, one aliquot of the residue sample was heated to 105 C to establish the water content of the residue; and another aliquot of the residue was heated to 180 C and then to 550 C to establish the level of unburned combustible material in the residue. The results of these tests are displayed on Table 2. One can not conclude from these data whether or not

TABLE 2 DETERMINATION OF PERCENT COMBUSTIBLES IN COMBINED RESIDUE

	ALIQUOT - 1	ALIQUOT - 2	
Sample	% Weight Loss at 105 C	% Weight Loss at 180 C	% Weight Loss 180 C - 550 C
1	25.73	31.87 28.17	2.58 1.91
2	26.88	18.68	1.46
3	29.61	26.04	2.01
Average	27.4	24.9	1.9
Composite *	23.64 23.63	29.02	2.33

* Composite of Gross samples 1, 2 and 3.

bonded water or anything else was driven off between 105 C and 180 C.

The test work on these samples was carried out by an independent laboratory. However, the system supplier (who is also the plant operator) purchased a drying oven capable of controlling oven temperatures up to 200 C, a furnace capable of maintaining controlled temperatures up to 1100 C, and an electronic balance capable of weighing samples to one milligram. This equipment is kept in the plant laboratory, and it is used to monitor the level of unburned combustibles in the residue on an ongoing basis.

TEST PROGRAM

In light of the diverse results described above, a program is underway in PTC 34 to develop an accurate and practical procedure to determine the unburned combustible content in the residue from combustion of municipal solid waste. The facility in New York State discussed above was selected as the site for this investigation because of the presence of the oven, furnace and balance.

Criteria for development of a new procedure included:

1. Use of the largest practical size sample (perhaps 1 to 2 pounds) to minimize or eliminate the need for size reduction of the sample. This criterion mandates the use of larger size equipment than has been customary for testing coal and coke.

2. Procedures designed to minimize biases or errors due to dewatering unspent sorbent, chemical breakdown of the products of reaction from an acid gas scrubber, and oxidation of metallic components of residue.

The procedure is under development based on the following underlying principle.

Underlying Principle

Combustibles in residue, when raised in temperature will volatilize the gaseous constituents so that the remaining combustible material is in the form of black, "fixed carbon" which then combusts in the presence of oxygen to form carbon monoxide or carbon dioxide; therefore, the visual absence of black pieces and specks in the residue is *the indication* that all of the combustibles in the residue have been driven off. The temperature at which black pieces and specks of fixed carbon disappear, indicating that combustibles have been driven off the ash residue from combustion, is significantly less than the temperatures customarily prescribed for ASTM test methods developed for coal and coke. (Charcoal which is preponderantly fixed carbon will ignite and burn at 650 F (345 C); and bituminous coal will volatilize its gaseous constituents and the fixed carbon will ignite and burn at 765 F (465 C). [3])

If it can be established that the temperature at which combustibles are driven off is lower than the temperatures at which non-combustible portions of the residue oxidize or decompose, then the weight loss during this process can be used as the measure of combustibles in the residue from combustion of municipal solid waste.

The following describes an experiment designed to verify the underlying principle.

The Experiment

Facility. The facility in New York State was selected as the site for the experiment to measure the moisture and unburned combustibles in residue. The facility is rated at 400 tons per day and it includes two 200-ton per day municipal solid waste incinerators. The incinerators are equipped with boilers sized to produce 70,000 pounds of steam per hour at 650 psig and 750 F, acid gas scrubbers, and 4-field electrostatic precipitators. Fly ash collected by the 4-field electrostatic precipitators is moved, by means of dry drag conveyors, (one for each incinerator) to a point where it can drop into ash extractors. The ash extractors are water impounded troughs that receive the bottom ash from the stoking grate as well as the fly ash from the electrostatic precipitator. The bottom ash and fly ash mix in the extractors. The mixed ash is slowly pushed up out of the water in the extractor and out of the extractor onto a vibrating conveyor. The vibrating conveyor receives the ash from both extractors, transports it out of one side of the boiler house where large objects are removed by means of a vibrating grizzly and the remaining ash is dumped onto a belt conveyor. The belt conveyor transports the ash to the ash storage building where it passes under a magnetic device to remove ferrous material and the remaining ash falls onto a pile on the loadout floor.

When. The experiment was conducted on November 23 and 24, 1992 with a final weighing and cleanup the morning of November 25.

Equipment. The facility was selected for the experiment because it was known that a drying oven capable of

controlling temperature up to 200 C and a furnace capable of controlling temperature up to 1100 C were available at the facility. A digital electronic balance was also available at the site capable of weighing to one-thousandths of a gram. It was not realized until the experiment began that the balance had a maximum capacity of 300 grams (about two-thirds of a pound). Therefore, it was not possible to work with the 1 to 2 pound samples originally planned.

Protocol. A Protocol for the experiment was prepared and circulated. The Protocol, finalized after the experiment, is included as an Appendix.

Procedure

The Residue Sample. A 20-gallon bucket was half filled with residue from the ash pile on the loadout floor. Special pains were taken to make sure that there was a considerable amount of unburned combustibles (paper) and metal in the sample. Portions of this sample were used for Runs One and Two. This means that the findings from the tests with regard to unburned combustibles, are probably higher than in the actual residue. Because the sample was taken from a pile on the floor, the moisture content was probably somewhat less than if a more representative sampling program had been undertaken.

Run One. The first sample was weighed at close to but less than 300 grams in an 8 inch by 8-inch aluminum foil pan (purchased in a package of six at a local supermarket) which was the maximum size that the oven would accept. The sample was placed in an oven set at 105 C, weighed at 15-minute intervals, stirred on occasion, until no further loss of weight was recorded. The oven was reset 25 C higher to 130 C and weighed at 15-minute intervals until no further weight loss was measured. The oven was reset 25 C higher to 155 C and this procedure repeated. Finally, the oven was set at 180 C and the same procedure repeated. The oven temperature was raised in increments of 25 C to determine if there was a temperature between 105 C and 180 C where bonded water was driven off. Photographs were taken periodically. (Although the temperature dial on the oven went to 200 C, the maximum temperature measured on a mercury thermometer that was centered in the top of the oven did not indicate much more than 180 C when the dial was set at 200 C.) A major portion of the contents of the 8-inch by 8-inch pan was dumped into a 6-inch by 3-inch aluminum pan (purchased in a package of six at a local supermarket) which was the maximum size that the furnace would accept. The pan was heated in the furnace to 300 C, weighed at 30-minute intervals until no further weight reduction was recorded. The oven temperature was increased to 400 C and successively to 500 C repeating the same procedure. The pan and sample were left in the oven at 500 C overnight. In the morning, after a final weighing at 500 C, some of the material remaining in the 3-inch by 6-inch pan was transferred to a 2-inch by 3-inch stainless steel pan (that happened to be available at the facility), weighed, and successively heated to 600 C, 700 C and 800 C. (The material was transferred from the aluminum pan to the stainless steel pan because aluminum melts between 600 and 700 C.) The results are displayed on Table 3 and Figures 1 and 2.

TABLE 3 DATA FROM RUN ONE

DATE	TIME	TEMP C	SAMPLE WEIGHT g	% OF WET WEIGHT	% WEIGHT LOSS FROM 105 C	% WEIGHT LOSS FROM 180 C
11/23	1015	105	276.7	100.0		
11/23	1030	105	267.7	96.7		
11/23	1045	105	257.7	93.1		
11/23	1100	105	250.6	90.6		
11/23	1115	105	241.6	87.3		
11/23	1130	105	233.9	84.5		
11/23	1145	105	225.9	81.5		
11/23	1200	105	219.1	79.2		
11/23	1215	105	212.7	76.9		
11/23	1230	105	207.9	75.1		
11/23	1245	105	204.0	73.7		
11/23	1300	105	201.4	72.8		
11/23	1315	105	200.0	72.3		
11/23	1330	105	199.6	72.1		
11/23	1345	105	199.0	71.9		
11/23	1400	105	198.9	71.9		
11/23	1415	105	198.9	71.9		
11/23	1430	105/130	199.0	71.9	0.0	
11/23	1445	130	198.7	71.8	0.2	
11/23	1500	130	198.5	71.7	0.3	
11/23	1515	130	198.5	71.7	0.3	
11/23	1530	130/155	198.5	71.7	0.3	
11/23	1545	155	198.3	71.7	0.4	
11/23	1600	155	198.2	71.6	0.4	
11/23	1615	155/180	198.2	71.6	0.4	
11/23	1630	180	198.2	71.6	0.4	
11/23	1645	180	198.1	71.6	0.5	
11/23	1700	180	198.0	71.6	0.5	
11/23	1715	180	197.9	71.5	0.6	
11/23	1730	180	197.9	71.5	0.6	
11/23	1745	180	197.9	71.5	0.6	
11/23	1800	300(1)	174.5	71.5	0.6	0.0
11/23	1830	300	weighed but not recorded			
11/23	1900	300	172.5		1.7	1.1
11/23	1915	300/400	172.5		1.7	1.1
11/23	1945	400	171.5		2.3	1.7
11/23	2000	400/500	171.2		2.5	1.9
11/23	2030	500(2)	169.5		3.5	2.9
11/24	0800	500	167.9		4.4	3.8
11/24	0823	600(3)	60.2		4.4	3.8
11/24	0900	600	60.2		4.4	3.8
11/24	1000	600	60.1		4.6	4.0
11/24	1100	700	59.8		5.1	4.5
11/24	1200	700	59.8		5.1	4.5
11/24	1300	800	59.9		4.9	4.3
11/24	1400	800	60.3		4.2	3.6

(1) From 1745 to 1800, transferred a portion of the sample from 8"x8" pan to 3"x6" pan and moved sample from oven to furnace.
(2) Left sample in furnace overnight (11.5 hours) at 500 C.
(3) From 0800 to 0823, transferred a portion of sample from 3"x6" aluminum pan to 2"x3" stainless steel pan.

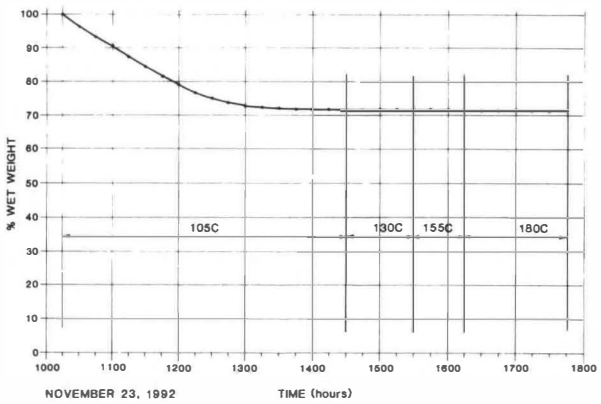

FIG. 1 DRYING RESIDUE—DATA FROM RUN ONE

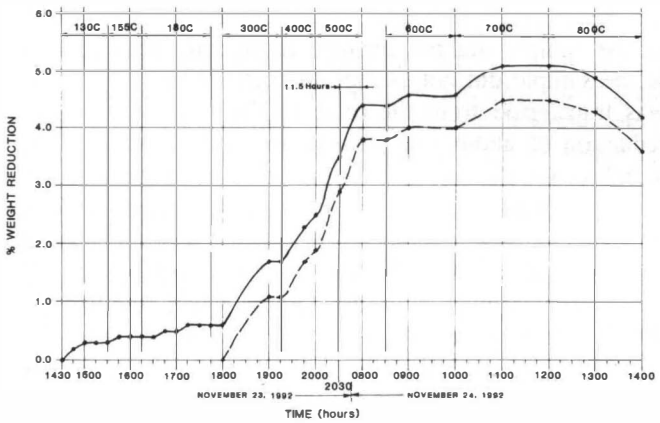

FIG. 2 WEIGHT REDUCTION AFTER STABILIZING AT 105 C AND 180 C—DATA FROM RUN ONE

Run Two. When the sample from Run One was removed from the oven and placed in the furnace, Run Two began. About 1 pound 4.5 ounces of residue was placed in an 8-inch by 8-inch pan and weighed on a postal scale. This pan was placed in the oven set at 105 C and left overnight. The next morning, the sample was removed from the oven. Since the ash had tended to congeal in large lumps, these lumps were broken up in the pan with a hammer. A portion of the sample was placed in an 8-inch by 8-inch pan and returned to the oven set at 105 C. The pan was weighed at 15-minute intervals until no further weight loss was measured. The sample was then returned to the oven set at 180 C. It was weighed repeatedly until it no longer lost weight. The sample was then set aside so that the oven could be used for Run Three. When the Run Three sample was moved from the oven to the furnace, the Run Two sample was returned to the oven set at 105 C. The sample was held in the oven until the furnace was available at the completion of Run Three. When the furnace was available, the Run Two sample was removed from the oven, weighed and a portion was transferred to a 3-inch by 6-inch pan and placed in the furnace, set at 550 C. After two hours and 20 minutes, the furnace setting was reduced to 105 C. The sample was left in the unopened oven until the next morning and then weighed. The results are displayed on Table 4.

TABLE 4 DATA FROM RUN TWO.

DATE	TIME	TEMP., C	SAMPLE WEIGHT, g	% WEIGHT REDUCTION FROM 105 C	% WEIGHT REDUCTION FROM 180 C
11/23	1850[1]	105	1 lb-4.5 oz		
11/24	0830[2]	105	255.5		
11/24	0900	105	254.9		
11/24	0915	105/180	254.9	0.0	
11/24	0930	180	254.1	0.3	
11/24	0945[3]	180	254.1	0.3	0.0
11/24	1300	105			
11/24	1900	105	254.6		
11/24	2130	105/550[4]	97.9	0.3	0.0
11/24	2350	550[5]			
11/25	0750	105	93.2	5.1	4.8

(1) Sample placed in 8"x8" pan and left in oven overnight (14.3 hours) at 105 C.
(2) Sample broken up and a portion transferred to another 8"x8" pan.
(3) Out of oven 0945 to 1300.
(4) Transferred a portion of sample from 8"x8" pan to 3"x6" pan and moved sample from oven to furnace.
(5) Reset temperature from 550 C to 105 C without opening furnace.

Run Three. A fly ash sample was obtained from the electrostatic precipitator drag conveyor before it was wetted. The fly ash was considerably darker than the mixed residue, but a few white lumps of lime were apparent. The sample filled about half a styrofoam coffee-cup. Sample weight was about 50 grams. The sample was poured into an 8-inch by 8-inch pan and placed in the oven set at 105 C. It was kept at this temperature until no further weight loss was detected and successively heated to 130 C, 155 C and 180 C to establish weight loss at these temperatures. The sample was then held at 105 C for about 1.75 hours until the furnace was available at the end of Run One. The sample was placed in a 3-inch by 6-inch pan and placed in the furnace at 300 C. The sample was weighed until no further weight loss was detected. It was successively heated to 400 and 500 C. At each temperature, the sample was weighed at 30-minute intervals until no further weight loss was detected. The sample was transferred from the 3-inch by 6-inch pan to the 2-inch by 3-inch stainless steel pan and heated to 600 C until no further weight loss was detected. The furnace temperature was increased to 750 C and held at this temperature for 1.75 hours. Weight loss was measured. The results are displayed on Table 5 and Figure 3.

TABLE 5 DATA FROM RUN THREE.

DATE	TIME	TEMP., C	SAMPLE WEIGHT, g	% OF 105 C WEIGHT	% OF 180 C WEIGHT
11/24	0850	Room	49.2	111.3	
11/24	1000	Room/105[1]	49.5	112.0	
11/24	1015	105	45.1	102.0	
11/24	1030	105	44.5	100.7	
11/24	1045	105	44.3	100.2	
11/24	1100	105	44.2	100.0	
11/24	1115	105/130	44.2	100.0	
11/24	1130	130	44.2	99.5	
11/24	1145	130/155	44.0	99.5	
11/24	1200	155	43.7	98.9	
11/24	1215	155/180	43.7	98.9	
11/24	1230	180	43.5	98.4	
11/24	1245	180/105[2]	43.5	98.4	
11/24	1425	105/300[3]	43.2	98.4	100.0
11/24	1500	300	42.8	97.5	99.1
11/24	1530	300/400	42.8	97.5	99.1
11/24	1600	400/500	42.9	97.7	99.3
11/24	1630	500	42.6	97.0	98.6
11/24	1700	500	42.5	96.8	98.4
11/24	1800	500	42.2	96.0	97.6
11/24	1830	500	42.1	95.9	97.5
11/24	1835	600[4]	37.1	95.9	97.5
11/24	1900	600	36.9	95.4	97.0
11/24	1930	600/750	36.8	95.1	96.7
11/24	2000	750	36.2	93.6	95.2
11/24	2115	750	35.7	92.3	93.8

(1) Sample placed in 8"x8" pan weighed and left at room temperature from 0850 to 1000 until the oven was available.
(2) Oven temperature reduced from 180 C to 105 C from 1245 to 1425 awaiting furnace.
(3) Sample transferred from 8"x8" pan to 3"x6" pan and moved from oven to furnace.
(4) Transferred most of sample from 3"x6" aluminum pan to 2"x3" stainless steel pan.

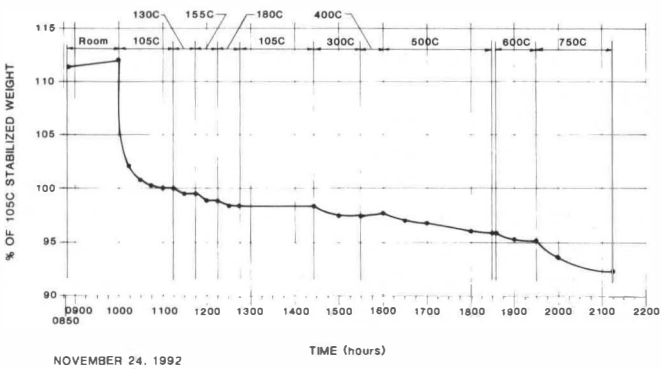

FIG. 3 WEIGHT REDUCTION OF FLY ASH STABILIZED AT 105 C— DATA FROM RUN THREE.

Discussion

General. Some eyebrows may be raised by those reading the test protocol with regard to departures from customary fuel laboratory procedures such as:

1. The use of aluminum baking pans purchased at a supermarket.
2. Weighing samples that have not been left to cool.
3. No mention of the use of desiccators or other means to inhibit moisture absorption by the samples prior to weighing.

These and other concerns were examined in detail during a development program for a test of 1 to 2 pound samples of refuse derived fuel and found to have a negligible impact on the validity of the test. [4]

Run One. During the drying stage of this sample, a 28 percent weight reduction was experienced over a four-hour period. The oven is equipped with a fresh air intake and vent to exhaust moisture and/or gases, and the sample was stirred on occasion to exposure new surface to the atmosphere in the oven. Once the weight of the sample was stabilized at 105 C, temperature in the oven was raised successively in 25 C increments to 130 C, 155 C and 180 C to determine if significant weight change occurred that could be attributed to non-combustion reactions. The total weight reduction while heating the sample from 105 C to a stabilized weight at 180 C was less than one percent. More weight was lost between 105 C and 130 C than for the other 25 C increments. The physical appearance of the sample did not change during this phase. Paper in the sample did not change in color. When the sample was transferred from the oven to the furnace, a weight reduction of about one percent was experienced at 300 C before weight was stabilized and a burning smell was noticed; whereas burning or other smells were not noticed at higher or lower temperatures. Thus, it would appear that the bulk of the volatiles were driven off at 300 C. The weight reduction of the sample when stabilized at 400 C was less than the weight reduction at 300 C. The weight reduction during the 500 C stage was the largest experienced in the furnace. At the end of the 500 C period, residue had an off-white color and was free of black specks which is the indication that all of the combustibles in the residue have been driven off. If one assumes that the volatiles are driven off of largely cellulosic material in the residue, a corellation could be developed between the heating value of the combustibles in the residue and the ratio of the weight reduction from 180 C to 300 C to the weight reduction from 180 C to 500 C. When the sample was further heated to 600 C and 700 C, the sample continued to loose weight. This is apparently due to non-combustion related chemical disassociation. However, during a final phase at 800 C, the sample gained weight. This was probably due to oxidation of some of the constituents of the residue. At completion of the 800 C run, the sample had taken on a greenish cast.

Run Two. Run Two was a simple test where the sample was dried overnight at 105 C and then heated to 180 C to establish the weight loss. The weight reduction when heated from 105 C to 180 C was half the weight reduction measured for Run One. This could be because of the protracted drying at 105 C. For both Runs One and Two, the weight loss from 105 C to 180 C was a fraction of one percent. A sample was then placed in the furnace

at the 550 C, the weight reduction was comparable to the weight reduction experienced during Run One at 500 C. At the end of the 550 C phase, the sample had an off-white color and was free of black specks. During the 500-550 C phase (for both Run One and Run Two), the remaining lumps in the sample tended to break down into a fine powder. Some lumps in the 1/4–1/2 inch size range remained. Several lumps were broken with a hammer to determine if unburned combustible remained within the lump. Some traces of black were observed. The level of black within the lump was far less than the overall level of black in the entire sample prior to the ashing procedure, thus the traces of black represent a very few percent of the unburned combustibles in the original sample.

Run Three. The sample used for this run was fly ash. The fly ash was ostensibly dry, as it had been taken from a dry conveyor shortly after it fell from the precipitator hoppers and before water was introduced to the process. The sample increased in weight by about one percent as it sat at room temperature for just over one hour. When placed in the 105 C oven, the sample quickly experienced a weight reduction of more than ten percent. It would seem that part of this weight loss could be loss of water of hydration in unreacted sorbent. The weight reduction of about 1.5 percent as the sample was heated successively to 130 C, 155 C and 180 C was greater than experienced in Runs One and Two, but far less than weight loss experienced at 105 C. As the sample was heated in the furnace to 300 C, 400 C and 500 C, the weight loss of 2.5 percent was less than the weight loss experienced in Runs One and Two. At 500 C, the sample started to form sticky lumps. At the high temperatures in the stainless steel pan, the sample, when stirred, had the consistency of a damp mush and sample took on a gray-green cast. (The green cast for Run Three was more pronounced than for Run One.) When the sample was cooled after the completion of the run, it "set up" in lumps that do not crush or crumble easily. When furnace temperature was increased from 600 C to 750 C, the sample experienced a pronounced weight loss (2.9 percent) which is probably due to chemical decomposition of the reaction products of the sorbent.

Equipment. The equipment used for the experiment included an oven with internal dimensions 10 inches wide by 10 inches high by 11 inches in depth, a furnace with internal dimensions of 4 inches wide by 4 inches high by 8 inches in depth, and a balance with a capacity of 300 grams and a linearity of ±0.002 grams. Catalog prices for this equipment are [5]:

Oven	$ 620.00
Furnace	1,175.00
Balance	1,095.00
Total	$2,890.00

A larger model of the furnace is available with internal dimensions of 9 inches wide by 9 inches high by 14 inches deep that could be fitted with an aspirator as described in D3174 and used to perform the function of both the oven and the furnace. (The aspirator requires drilling two holes in the furnace, a few small diameter pipe fittings, and the availability of compressed air.) A larger capacity model of the same balance is available with a capacity of 3,000 grams and a linearity of ±0.1 gram. Prices from the same catalog for the larger capacity equipment are:

Furnace	$ 1,585.00
Balance	850.00
Total	$2,435.00

With the larger capacity equipment, a 1 to 2 pound sample could be placed in an $11\frac{3}{4}'' \times 8\frac{1}{2}'' \times 1\frac{1}{4}''$ aluminum pan, dried and ashed at temperatures up to 550 C in the same pan. Baking pans of this or similar size may be purchased in packages of two for less than $2.00 in most supermarkets. The aluminum pans can be reused. (The porcelain crucibles used in fuel laboratories to ash 1 gram samples of coal, coke or residue cost about $6.00 each. They can be reused.)

CONCLUSIONS

At this point in the investigation, several conclusions can be drawn:

1. There is a need for a new standard test method to measure the combustibles in residue from combustion of municipal solid waste because:

   a. Test methods presently used for other solid fuels require a degree of analysis sample preparation that is not practical for residue from combustion of municipal solid waste.

   b. Test methods presently used for other solid fuels are carried out at high temperatures that induce reactions in the non-combustible portion of the residue that confound the unburned combustible measurements for residue from combustion of municipal solid waste.

2. Small but significant reactions occur between 100 C and 180 C in residue from combustion of municipal solid waste that are not combustion related.

3. The combustibles in residue from combustion of municipal solid waste are driven off at temperatures up to and including 500 C. (This is not to say that it is established that reactions do not occur that are not combustion related.)

4. Reactions that are not combustion related occur in the residue from combustion of municipal solid waste at temperatures above 500 C.

5. Data accumulated thus far suggest that weight loss between 180 C and 500 C may be a valid measure of

combustibles in the residue from combustion of municipal solid waste.

6. More data is required, therefore a test protocol is offered as an Appendix for those who test the residue from combustion of municipal solid waste to use and report their findings and comments to PTC 34.

ACKNOWLEDGEMENTS

The author is indebted to the members of PTC 34 for encouragement and suggestions as this paper evolved. He is particularly grateful for the review provided by:

R. John Briggs, Foster Wheeler Ltd.

Gregory Gesell, P.E., American Ref-Fuel

Franklin A. Hamlyn, P.E., Wheelabrator Technologies, Inc.

Herbert I. Hollander, P.E., Consultant at Large

John K. Kieffer, semi-retired from a career dedicated to laboratory analysis of solid fuels and their residue after combustion.

Steven A. Scavuzzo, The Babcock & Wilcox Company

Zenon Semanyshyn, Ogden Martin Systems

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[3] Steam/Its Generation and Use, 40th Edition, S.C. Stultz and J. E. Kitto; eds., The Babcock & Wilcox Company, Barberton, Ohio, 1992, p. 9-9.

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APPENDIX
TEST METHOD FOR DETERMINING MOISTURE, COMBUSTIBLE CONTENT, AND HEATING VALUE OF RESIDUE FROM MUNICIPAL SOLID WASTE INCINERATORS

1. Scope

This test method is a draft procedure to determine the moisture, combustible content and heating value of residue from municipal solid waste incinerators. The procedure is designed to use a large sample size of 0.5–1 kg for analysis. This procedure does not address how to obtain a representative sample.

2. Summary of Test Method

Moisture content is determined by weighing the residue before and after drying the residue under controlled conditions of sample weight, time, temperature and equipment. The moisture content is equivalent to the loss of weight of the sample during the drying process.

Combustible content is determined by weighing the dried residue obtained from the moisture content determination before and after ashing the dried residue under controlled conditions of sample weight, time, temperature and equipment. The combustible content is equivalent to the loss of weight of the sample during the ashing process.

Note: This draft procedure ignores time and atmosphere aspects, in anticipation that the impact from these items are small enough to ignore, with the goal of not making the procedure so complicated it cannot be completed in the field.

3. Significance and Use

The moisture content determined by this method is the moisture contained in the residue after processing in the residue handling system of a municipal incinerator. The combustible content determined by this method is the combustible remaining in the residue from a municipal incinerator. These values can be used for thermal efficiency calculations and performance guarantee purposes. There is no ASTM Standard Method to determine the combustible content of residue from combustion. In an attempt to overcome the difficulty of obtaining a small sample representative of the entire residue stream, this method utilizes a larger sample than is used for most other procedures. Metal, glass, and other non-combustible components remain in the test sample. The method is designed to minimize the effects of any chemically bonded water, carbonates, metal oxidation, and other factors which can confound other test methods.

4. Apparatus

4.1. Electric Muffle Furnace. The furnace shall be large enough to accommodate a 0.5–1 kg sample comfortably. Internal dimensions of 9 inches wide by 14 inches long should be adequate. Temperature shall be capable of being regulated between 100 to 600 C. It shall be equipped with a temperature indicator and means of controlling the temperature within the specified limits. Adequate ventilation of off gases shall be provided. Temperature throughout the furnace shall be maintained within the specified temperature limits. A modification as described in ASTM D3174 should be adequate.

4.2 Sample Pan. Aluminum pans adequately sized to safely contain a 0.5–1 kg sample and allow stirring without spillage. Supermarket baking pans $11\frac{3}{4}'' \times 8\frac{1}{2}'' \times 1\frac{1}{4}''$ should be adequate.

4.3. Balance. Sensitive to at least 0.1 g. The balance shall be capable of weighing hot samples or be fitted with an insulating pad in such a manner to prevent damage to the balance while allowing accurate measurement.

4.4 Container Tongs. Device to hold and carry container in a safe manner while hot. Ordinary kitchen tongs should be adequate.

4.5. Insulated Gloves. Suitable for the timid when handling a heated sample with tongs.

5. Procedure

5.1. Weigh the empty sample pan and record this weight as the pan weight, A. Place the thoroughly mixed residue sample in the pan. The residue sample shall weigh 0.5–1 kg. and fit easily in the weighed sample pan, leaving enough room to prevent spillage when handling. An average depth of about 1 cm has been found to be suitable. Weigh the sample in the pan before placing in the furnace. Record this weight as the residue sample wet weight, B.

5.2. Place the sample pan in the furnace chamber set at *180* C for two hours. Weigh the sample, stir the sample, and return it to the furnace. Hold at *180* C for fifteen minutes and weigh the sample again. Repeat the weighing, stirring and holding process every fifteen minutes at *180* C until a constant sample weigh is reached (±0.1 g). Record this weight as the residue sample dry weight, C.

5.3. Once a constant residue sample dry weight is obtained, raise the furnace temperature to *500* C and hold for two hours. Remove the sample from the furnace, stir and inspect for any remaining black carbon specks. Weigh the sample and return it to the furnace. Continue holding at *500* C for 30 minutes and weigh the sample again. Repeat the weighing and holding process every 30 minutes at *500* C until a constant sample weigh is reached (±0.1 g.) Record this weight as the residue sample dry ash weight, D.

6. Calculation

6.1. Calculate the moisture percent in the residue sample as follows:

$$\text{moisture in residue sample, \%} = \left(\frac{B-C}{B-A}\right) \times 100 \qquad (1)$$

where:

A = weight of pan, g
B = weight of pan and wet residue sample, g
C = weight of pan and dry residue sample, g.

This percentage may be used to establish the net weight of dry residue produced during a test.

6.2. Calculate the combustible percent in the dry residue sample as follows:

$$\text{combustibles in dry residue sample, \%} = \left(\frac{C-D}{C-A}\right) \times 100 \quad (2)$$

where A and C are defined above, and D = weight of pan and ashed residue sample, g.

This percentage may be used to establish compliance with a guarantee of percent combustibles in the residue.

6.3. Calculate the heating value of the residue sample as follows:

$$\text{heating value, Btu/lb} = \frac{\text{dry combustibles \%} \times 12,000}{100} \qquad (3)$$

where dry combustible %, is from Equation 2 above. *12,000*, is an approximation of the heating value of the combustible portion of the residue in Btu/lb from E 955.

This heating value may be used to establish the heat lost due to unburned combustibles in the residue.