REVIEW OF COMBUSTION-- COULOMETRIC CO_2 DETECTION METHOD FOR DIRECT DETERMINATION OF CARBON ON METAL SURFACES

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ABSTRACT

The method proposed in 1979 for direct determination of carbon on steel and other metal surfaces has been tested and used routinely by several laboratories. The experiences of these laboratories and additional work to demonstrate the validity of the method are discussed. The method uses an oxygen atmosphere at $\leq 580^\circ C$ to oxidize organic and elemental carbon from metal surfaces. CO_2 formed during the oxidation of samples is detected coulometrically. Carbon within steel samples is not oxidized. The accuracy of the technique is ± 0.02 mg C/ft^2 (0.2 mg C/m^2). The direct oxidation method is faster and easier to use than indirect methods and gives more accurate results.

INTRODUCTION

The dependence of surface coating quality on surface cleanliness has been demonstrated by a number of investigators (1)(2)(3). It has been shown that carbon containing surface contaminants cause voids and defects in phosphate pretreatment layers for steel coils (4). The changed morphology and surface coverage of the zinc phosphate plating results in premature failure of protective surface coatings(5). Determination of surface carbon contamination has become a standard industry practice since a number of studies have confirmed the correlation between surface carbon and corrosion resistance as measured by salt fog tests(4)(6). The carbon containing contaminants may be from a number of sources including rolling oils and amorphous or graphitic carbon deposited by pyrolysis during annealing.

Prior to this time the only widely accepted method for determination of carbon in surface contaminants has been to swab samples with a hydrochloric acid(HCl) solution and determine the amount of carbon transferred onto the swab(4)(7)(8).

In 1978 a new method for determination of surface carbon was proposed in an attempt to simplify the analysis so that it would be easier to use for quality assurance testing of materials(9). Other goals of the new method are to reduce analysis times and to increase the accuracy and reliability of the test. This method involves the direct oxidation of surface carbon to CO_2 followed by coulometric detection. Several laboratories are now using the direct oxidation method and this paper reports their experiences and results of additional work to demonstrate the validity of the method. Also included are references to similar work which were previously overlooked and add to the data supporting direct oxidation methods(10)(11)(12).

EXPERIMENTAL

HCl Swab Method

Samples 12 in.(300mm) x 12 in.(300mm) were swabbed with glass fiber filter papers saturated with 50% HCl until no further colored material could be removed. The HCl and water were driven from the swab by heating to 180°C for one hour. The swab and residue were analyzed for carbon using a Leco CS46 combustion apparatus equipped with an infared detector.[1]

Direct Oxidation Method

The apparatus used, shown in figure 1, is manufactured by Coulometrics, Inc.[2] and consists of a combustion apparatus and coulometer for automatic titration of CO_2. The combustion apparatus includes an oxygen prepurification train, furnace containing horizontal combustion tube, sample introduction port and scrubber train for removal of potentially interfering gases. The combustion tube contains barium chromate as both an oxidation catalyst and scrubber for sulfur oxides and hydrogen chloride. Silver, for scrubbing hydrogen bromide and hydrogen iodide, is also in the combustion tube. Following the combustion tube is a nitrogen oxide scrubber using the following components: Magnesium perchlorate for water vapor, acid dichromate($K_2Cr_2O_7+H_2SO_4$) on a diatomaceous earth substrate to oxidize nitrogen oxides(NO_x) to nitrogen dioxide(NO_2) and manganese dioxide to absorb NO_2. The CO_2 coulometer incorporates a cell where CO_2 is quantitatively abosrbed and titrated. The result is displayed directly in micrograms of carbon. Huffman(13) has discussed the performance of the coulometer.

Samples were prepared by cutting them into strips approximately 0.4 in.(10mm) x 4 in.(100mm) and a 0.25 in. (6.4mm) hole punched at one end of each strip. Figure 2 illustrates the ladle and sample configuration used to introduce samples into the combustion zone.

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[1] Leco Corporation,3000 Lakeview Ave., St. Joseph, Michigan 49085

[2] Coulometrics, Incorporated, P.O. Box 544, Wheat Ridge, Colorado 80033

For each analysis 4 strips of sample were attached to the ladle and placed in the cool zone of the combustion tube. The introcustion port was closed and oxygen allowed to sweep out CO_2 which may have entered the system while samples were being inserted. Following the 60 second sweep period the coulometer was set to 0 micrograms of carbon and the sample pushed into the combustion zone using the external magnet. After all CO_2 has ceased evolving (5 to 8 minutes) the number of micrograms of carbon evolved was recorded and the sample removed. The surface contamination was calculated by dividing the number of micrograms of carbon found (corrected for blank) by the area of samples tested. Clean samples for use in blank determinations and other tests were prepared by heating strips of steel to 580°C for 10 minutes.

To differentiate between carbon species easily oxidized and those more difficult to oxidize the instrument was modified by adding a second furnace and the sample introduction system was adapted so that a sample could be moved into either furnace to permit use of two combustion temperatures.

RESULTS AND DISCUSSION

Typical results of the direct oxidation method are shown in Table 1.

Sample	Results[a]	Mean[a]	Std. Deviation[a]	%Std. Devi.
1	1.55,1.40,1.49,1.61	1.51	0.08	5.3
2	0.44,0.61,0.92,0.93, 0.41,0.57	0.65	0.21	32.3
3	1.56,1.19,1.29	1.35	0.16	11.9
4	1.02,1.02,0.85,1.06	0.99	0.08	8.1
5	1.02,0.99,1.18,0.91	1.03	0.10	9.7
6	1.03,1.34,1.10,1.48	1.24	0.17	13.7
		avg.	0.13	13.5

[a] Values in mg C/ft^2; multiply by 0.011 to convert to g C/m^2.

The variation in results shows that sample homogenity limits the accuracy rather than the instrument capability which is approximately ±0.2 µgC or ± 0.02 mgC/ft^2 (0.2 mg C/m^2) for approximately 13 square inches of sample surface. Table 2 shows typical results for the HCl swab method and illustrates that uncertainty in HCl swab results for its larger samples is comparable to the direct oxidation result uncertainty.

Table 2

Direct oxidation and Replicate HCl swab results for several cold-rolled steel samples.

Direct Oxidation	HCl Swab Results[a]			Mean	Std. Devi.	%Std. Devi.
0.46	0.54	0.42	0.15	0.37	0.16	43.2
1.27	1.08	0.67	0.57	0.77	0.22	28.6
1.30	0.54	0.84	0.45	0.61	0.17	27.9
0.70	0.52	0.37		0.45	0.08	17.8
2.30	0.43,	0.27,	0.73	0.48	0.19	39.6
				avg.	0.16	31.4

[a] Results from first 3 samples are from independent laboratories. Results on last 2 samples are within 1 laboratory.

Sample inhomogentiy limits the analysis accuracy but results are still pracitical for quality assurance testing. However, a new furnace is to be used in future models of the instrument which will permit use of samples up to 0.75" x 7"(1.9 cm x 18 cm). This will permit sample areas to be increased from under 13 square inches(81 cm^2) to 42 square inches(270 cm^2) when using four strips of sample. It will also be possible to place two furnaces side by side so that samples up to 0.75" x 11"(1.9 cm x 28 cm) may be used to give total sample areas of 66 square inches(425 cm^2). With the large sample sizes sample homogenity problems will be minimal and accuracies proportionately improved. An additional benefit of using the second furnace would be that one furnace would be used for heating the combustion catalyst only and so it could be operated at a temperature more ideal for the combustion catalyst. Catalyst efficiency is discussed further later in this paper.

COMPARISON OF SURFACE CARBON RESULTS OBTAINED BY THE HCl SWAB/LECO 46 COMBUSTION METHOD AND DIRECT OXIDATION/CO_2 COULOMETER METHOD

TABLE 3

Number of Samples	Average Surface Carbon* Value (X_A) by the HCl Swab/ Leco 46 Method	Average Surface Carbon*Value (X_B) by the Direct Oxidation/CO_2 Coulometer method	X_B-X_A
25	0.14	0.71	0.57
25	0.16	0.75	0.59
25	0.26	0.74	0.48
25	0.27	0.86	0.59
29	0.20	0.53	0.33
24	0.63	1.51	0.75
20	0.29	0.87	0.58
			0.56**

*Surface carbon value in units of $mg/ft.^2$. Multiply mg/ft^2 by 10.6 to convert to mg/m^2.

**Average mean difference of the two methods.

Data provided by Phillip L. Coduti, Inland Steel Research Laboratories, 3001 E. Columbus Dr., E. Chicago, Indiana and presented at Corrosion/80(5)

Tables 2 and 3 illustrate the difference in results between the HCl swab and direct oxidation methods. The direct oxidation results are consistently higher and great effort has been made to identify the reason(s).

The two most likely causes of low results for the HCl swab method were identified as failure to remove carbon containing contaminants from the surface and loss of volatile organics during the drying and HCl elimination. Direct oxidation testing of samples which had been swabbed for the HCl swab test showed only small amounts of carbon are left on the metal surface following the acid"cleaning" for carbon extraction--the amount was not significant compared to the differences in results for the two methods. To examine the potential loss of volatile organics during the HCl elimination adjacent samples were taken from coils so that replicate analyses could be performed. One set of samples were analyzed using the standard HCl swab method. The second set of samples were analyzed using the HCl swab method except that the swab was dried in vacuum without heating. When this was done results were comparable to the results obtained for adjacent sections tested using the direct oxidation method. Further testing showed that the amount of loss of organic carbon varied with drying time and temperature and that ovens used for drying in some laboratories provided uneven heating of the crucibles.

When crucibles from previously confirmed "dirty" samples were heated longer than the prescribed time in some cases virtually all carbon was lost from the swab. The presence of volatile organic materials on the surfaces was confirmed by heating samples to 180°C, passing the carrier gas stream flowing over the samples through an oxidation catalyst and to the CO_2 detector. Table 4 summarizes results of this test. The amount of CO_2 detected was comparable to the difference in results between the direct oxidation and HCl swab methods.(5)

TWO-STAGE OXIDATION USING THE DIRECT-OXIDATION/CO_2 COULOMETER METHOD

Table 4

Sample	180°C	600°C	Total
Shipping Oil	Very Volatile	Total Combustion	--
Graphite	None	Total Com-	--
"Low" Surface Carbon Steel	0.21 mg/ft^2	0.33 mg/ft^2	0.54 mg/ft^2
"High" Surface Carbon Steel	0.74 mg/ft^2	0.58 mg/ft^2	1.32 mg/ft^2

Multiply mg/ft^2 by 10.6 to convert to mg/m^2

Data provided by Phillip L. Coduti, Inland Steel Research Laboratories, 3001 E. Columbus Dr. E. Chicago, Indiana and presented at Corrosion 180(5)

The possibility that the higher direct oxidation results were due to carbon from within the samples reacting has been considered(9). The ≤580°C temperature used was selected by obtaining a plot of CO_2 evolved is temperature and extrapolating to identify where carbon from within steel would not be expected to react. Blanks determined using previously tested samples are no higher than those obtained using no sample. Boggs and Lee also address this question and note that reaction of carbon from within steel samples would be limited by the diffusion rate of the carbon within the steel.(10)(11). Lee reports a contribution of 6 micrograms of carbon per square inch(0.86 mg/sq. ft or 9.2 mg/m^2)(11). As reported previously the author has seen evolution of CO_2 from carbon within the sample at 600°C but not at 580°C and the required combustion period when using Coulometric detection is five minutes or less. Boggs reported neglible reaction of carbon from within steel samples when using 10 minute combustion periods at 500°C(10).

Lee prepared samples for blank determinations by using an abrasive jet spray of alumina and water(11). This technique of sample preparation is probably desirable for blank determinations but was not used because of difficulties obtaining the equipment and further blank studies did not appear warranted.

When the method was proposed a question was raised about the efficiency of the barium chromate($BaCrO_4$) combustion catalyst used. The laboratories using the technique are all still using the $BaCrO_4$ and report good recoveries of standards. Standards are tested by 1) weighing organic standards such as benzoic acid in platinum boats and introducing them into the combustion furnace with appropriate ladles, 2) coating organic materials such as steoric acid on metal samples by first dissolving them in volatile solvents, placing a measured amount of the solution on samples and allowing the solvent to evaporate off prior to analyzing the sample. Samples of rolling oils used have also been used as standards and test samples. The catalyst may not be critical because a pure oxygen atmosphere is used and the metal surface may catalyze the oxidation reaction. When larger samples are used the increased amount of organics to be oxidized may require a better catalyst or use of the $BaCrO_4$ at a higher temperature. If a single zone furnace is used copper oxide(CuO)or silver vanadate can be used to ensure complete oxidation. $BaCrO_4$ has been used in spite of its potential inefficiency because it also serves as an excellent SO_2/SO_3 scrubber should there be sulfur species in the surface contaminants. Sulfur species are not expected however on cold rolled steel samples and significant amounts of sulfur have not been seen on samples studied by secondary ion mass spectroscopy(SIMS)(5).

Because of an interest in determining the nature of contaminants on the surface an instrument was set up to permit analysis of samples using two combustion temperatures The goal was to differentiate between organic and elemental carbon on the surface. Work done by others attempting to differentiate between organic and elemental carbon on non-metal samples showed that it can be done by using two combustion temperatures(14)(15)(16). It was found that 450°C was adequate to oxidize organics on metal surfaces without oxidizing amphorphous carbon or FeC on the metal surface. Using 450°C to oxidize organics from the surface then moving the samples to the 580° C for determination of non-organic carbon on the surface showed that for cold rolled steel samples 85-90% of the surface carbon was organic. Lee suggests temperature programming for identification of the nature of the contaminant(11). Using SIMS and other surface analysis techniques the non organic carbon for action was identified as being essentially all amporphous carbon, no crystalline or graphitic carbon was seen and only a small amount of FeC was found.

Since elemental carbon was seen on metal surfaces tests were performed which showed that graphite and soot are oxidized from the metal surfaces at ≥550°C.

SUMMARY

The proposed method for direct determination of carbon on steel and other metal surfaces has been extensively tested and routinely used by several laboratories[3]. Results obtained demonstrate that by using combustion temperatures of less than 600°C reliable data can be obtained and that carbon from within metal samples does not interfere. Although the data reported is on cold rolled steels the method has been used for other metals including, stainless steel, aluminum, galvanized steel and nickel without difficulties. Some metals can be analyzed using higher combustion temperatures if desired or lower temperatures may be used so that organic contaminants only are detected. The method meets the goals of being fast(less than 10 minutes), easy to perform and is at least as accurate and reproducible as all other methods in use at this time.

Comments from those using the method include: 1) "Very good starting point... The instrument is doing and responding as described... much easier and better than the Ford method" 2) "...Highly suitable, good for pretreated, galvanized, aluminum..." 3)"... used in quality check of incoming material... has alreacy (after 3 months use) saved a great deal of money and inconvenience by enabling us to identify one supplier as providing

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[3] Names of laboratories using the technique are available from Coulometrics, Inc., P.O. Box 544, Wheat Ridge, Colorado 80033

contaminated material probably from a foreign source... 4) "... galvanized and porus samples... no other technique works" 5) "Run both ways still only because of Ford.... Also able to use on other types of samples such as coke." 6) "used to test cleaner efficiency – Variation with temperature and contamination... 7) Only problem is preparing samples(preliminary wash and cutting to size)... larger samples would simplify and perhaps resolve Ford's objection.

The consensus is that the method is fast and easy to perform without special skills and that setting up for the method is less expensive than the HCl swab method using the Leco CS46 carbon analyzer(approximately $8,000 vs $28,000 In addition to the basic instruments laboratories must obtain a pretreatment washer for samples and a die and punch to cut out samples). The only proposal for improving the instrument is changes to permit larger samples.

Because of its lower cost, both initial expense and operation, and ease of use the direct oxidation method appears to offer a substantial benefit for all having to test for surface contamination.

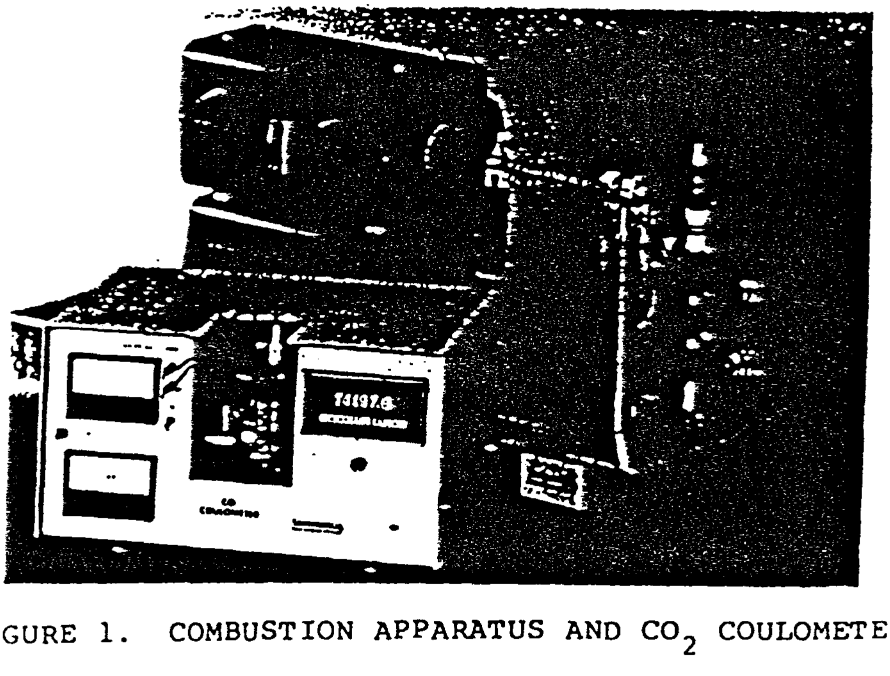

FIGURE 1. COMBUSTION APPARATUS AND CO_2 COULOMETER

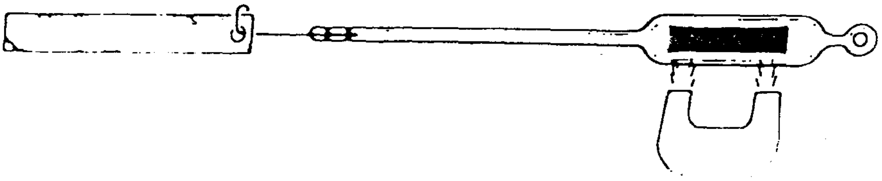

FIGURE 2. LADLE AND SAMPLE

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