



# TECHNICAL PAPER

## INDEX TERMS

Carbon  
Carbon Dioxide

## DIRECT DETERMINATION OF CARBON ON METAL SURFACES

By

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### ABSTRACT

A method for the direct determination of carbon on steel and other metal surfaces has been developed. Organic materials and some forms of elemental carbon on the surface are oxidized or volatilized at 580°C in an oxygen atmosphere. The gases are swept into an oxidation catalyst where they are oxidized to carbon dioxide (CO<sub>2</sub>). After removal of potentially interfering substances the CO<sub>2</sub> is determined using a CO<sub>2</sub> coulometer. It was found that at temperatures below 600°C carbon contained in steel is not oxidized. The accuracy of the method is  $\pm 0.02\text{mg C/ft}^2$  ( $0.0002\text{g C/m}^2$ ). Recoveries of carbon by the new method were higher than with indirect techniques. The direct method is faster and easier to use than the indirect methods.



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## ABSTRACT

A method for the direct determination of carbon on steel and other metal surfaces has been developed. Organic materials and some forms of elemental carbon on the surface are oxidized or volatilized at 580°C in an oxygen atmosphere. The gases are swept into an oxidation catalyst where they are oxidized to carbon dioxide (CO<sub>2</sub>). After removal of potentially interfering substances the CO<sub>2</sub> is determined using a CO<sub>2</sub> coulometer. It was found that at temperatures below 600°C carbon contained in steel is not oxidized. The accuracy of the method is  $\pm 0.02\text{mg C/ft}^2$  ( $0.0002\text{g C/m}^2$ ). Recoveries of carbon by the new method were higher than with indirect techniques. The direct method is faster and easier to use than the indirect methods.

## INTRODUCTION

During the manufacture and handling of sheet metal the surfaces may become contaminated by a variety of materials. These contaminants may interfere with the adhesion of surface coatings and reduce corrosion resistance. It is desirable to test all lots of material to determine the extent of surface contamination.

Hospadaruk(1) has shown a correlation between the surface carbon contamination and corrosion resistance. The carbon may be from surface oils or amorphous carbon or graphitic carbon deposited by pyrolysis during coil annealing. A procedure in current use(1) to determine surface carbon on steel is to swab samples with a glass fiber filter paper saturated with 50% hydrochloric acid (HCl). The HCl is driven off and the carbon residue on the swab determined. Surface contamination has also been determined by washing samples with chloroform, evaporation of the chloroform and weighing the residue. Both the chloroform wash and the HCl swab methods suffer from long analysis times, potential loss of volatile components and incomplete removal of surface contaminants.

This paper describes a new method for determination of surface carbon using direct oxidation of surface contaminants to CO<sub>2</sub>. The CO<sub>2</sub> formed is determined by coulometric titration. Interference from carbon within steel does not occur. The method is rapid, simple to perform and does not risk loss of volatile components or incomplete removal of contaminants.

## EXPERIMENTAL

### Chloroform Wash/Weigh Method

Samples 12in. (300mm) x 12in. (300mm) were washed with chloroform and the chloroform and all particles removed collected. The chloroform was evaporated and the residue weighed. The weight of the residue was determined to within 0.5mg.

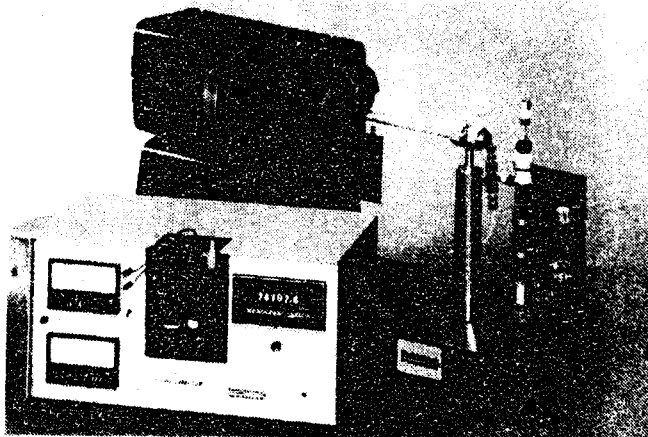


FIGURE 1. COMBUSTION APPARATUS AND CO<sub>2</sub> COULOMETER

#### HCl Swab Method

Samples 12in. (300mm) x 12in. (300mm) were swabbed with glass fiber filter papers saturated with 50% HCl until no further colored material could be removed. The HCl was driven from the swab by heating to 200°C for 30 minutes. The swab and residue were analyzed for carbon using a Leco CS46 combustion apparatus equipped with an infrared detector.

#### Direct Oxidation Method

The apparatus used, shown in figure 1, is manufactured by Coulometrics, Inc.<sup>2</sup> and consists of a combustion apparatus and coulometer for automatic titration of CO<sub>2</sub>. The combustion apparatus consists of 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 and chlorine. Silver, for scrubbing bromine and iodine, 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 on a diatomaceous earth substrate to oxidize nitrogen oxides (NO<sub>x</sub>) to nitrogen dioxide (NO<sub>2</sub>) and manganese dioxide to absorb NO<sub>x</sub>. The CO<sub>2</sub> coulometer incorporates a cell where CO<sub>2</sub> is quantitatively absorbed and titrated. The result is displayed directly in micrograms of carbon. Huffman(2) has discussed the performance of the coulometer.

<sup>1</sup>Leco Corporation, 3000 Lakeview Ave., St. Joseph, Michigan 49085

<sup>2</sup>Coulometrics, Inc., P.O. Box 544, Wheat Ridge, Colorado 80033

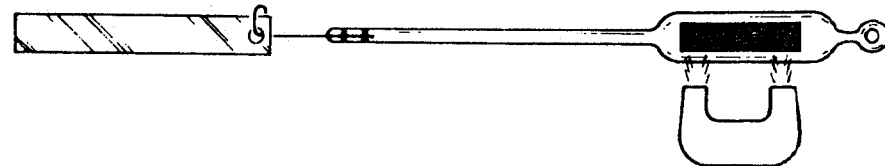


FIGURE 2. LADLE AND SAMPLE

Samples were prepared by cutting them into strips approximately 0.4in. (10mm) x 3in. (76mm) and a 0.25in. (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.

For each analysis 4 strips of sample were attached to the ladle and placed in the cool zone of the combustion tube. The introduction port was closed and oxygen allowed to sweep out CO<sub>2</sub> 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<sub>2</sub> had ceased evolving (6 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 sample 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 determine the optimum analysis temperature cleaned samples and samples containing 1 mg C/ft<sup>2</sup> (0.01g C/m<sup>2</sup>) were analyzed by operating the main furnace at 1000°C and using an auxiliary furnace to heat the samples. Following the sweep period the analysis was begun with the positioning of the auxiliary furnace which was heated to 100°C over the samples. The temperature was increased in 100°C increments every 8 minutes. The coulometer readout was recorded every minute. Results obtained were corrected for a system time blank which was obtained by observing the number of micrograms of carbon titrated during a 15 minute period with no sample in the apparatus.

Recovery determinations were performed using commercial grade dioctyl sebacate coated on cleaned cold-rolled steel samples and on primary standard grade benzoic acid and sulfonilamide weighed into platinum boats. The amount of dioctyl sebacate applied was determined by weighing the samples before and after application of the dioctyl sebacate. The weight of dioctyl sebacate was determined to within 3%. The benzoic acid and sulfonilamide weights were determined to within 0.1%.

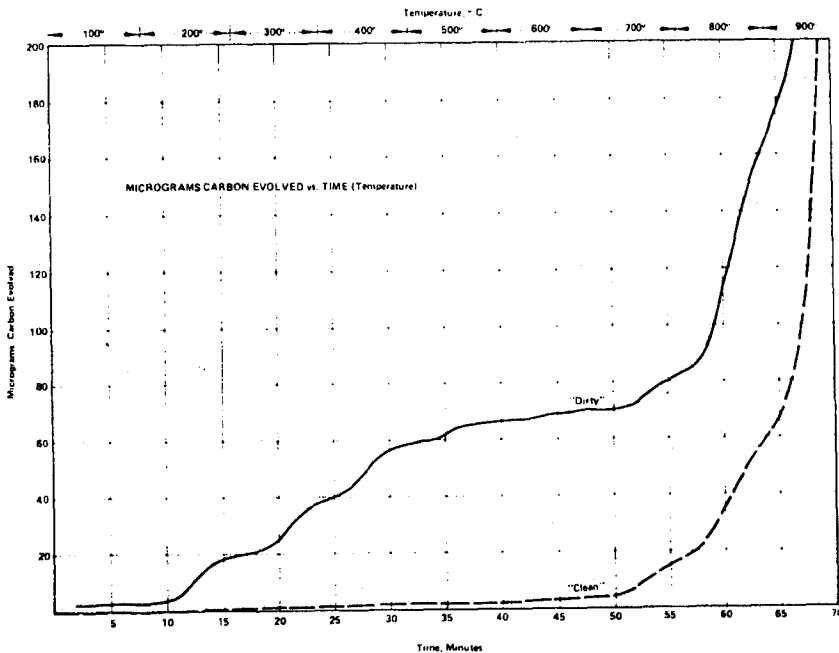


FIGURE 3. MICROGRAMS CARBON EVOLVED VS TIME (TEMPERATURE) FOR COLD-ROLLED STEEL SAMPLES.

RESULTS AND DISCUSSION

A plot of the data obtained in the micrograms of carbon evolved vs time (temperature) study is shown in figure 3. The system time blank correction used was 0.2 micrograms of carbon per minute. A slow release of CO<sub>2</sub> from compositional carbon is shown to begin at 600°C for the clean sample. The blank due to the sample was 4 micrograms of carbon at the end of the 600°C interval (48 minutes). Additional tests showed that at 580°C the total blank was 2.5 micrograms of carbon for an 8 minute analysis. Comparable blank values are obtained for samples which do not contain potentially interfering carbon. The reproducibility of the blank restricts the detection limit and accuracy of the method to approximately 0.02mg C/ft<sup>2</sup> (0.0002g C/m<sup>2</sup>).

The curve for the "dirty" sample in figure 3 is horizontal at the end of the 600°C time interval indicating that all oxi-

dizable surface carbon had been oxidized. Any remaining surface contamination is not detectable because use of a higher combustion temperature will oxidize carbon within the steel.

Extrapolation of the rate of evolution of CO<sub>2</sub> from the cleaned and "dirty" samples above 600°C indicates that oxidation of compositional carbon is not expected below 600°C. Therefore, the method of cleaning samples for blank determinations is believed to be acceptable. If compositional carbon is oxidized in the cleaning process the blank correction would be erroneously low and yield high surface contamination results.

Surface contamination values obtained for a number of cold-rolled steel samples are listed in table 1. Direct oxidation results are an average of 0.74mg C/ft<sup>2</sup> (0.0081g C/m<sup>2</sup>) higher than the values obtained by the HCl swab method suggesting the HCl swab method may fail to detect significant amounts of surface carbon contamination. The poor correlation Hospadaruk(1) found between surface carbon contamination and salt spray failure times for phosphated and painted samples may also suggest the poor recovery of the HCl swab method he used. For the difference in values between the direct oxidation method and HCl swab method to be due to oxidation of compositional carbon an average of 48 micrograms of carbon would be being oxidized from within the samples. This appears unlikely but it would be desirable to obtain clean samples by other cleaning techniques to confirm that compositional carbon does not react. It was not possible to obtain samples cleaned by other methods during this study.

TABLE 1

RESULTS OBTAINED FOR COLD-ROLLED STEEL SAMPLES BY 3 METHODS

<u>Direct Oxidation</u> <sup>a</sup>	<u>HCl Swab</u> <sup>a</sup>	<u>Chloroform Wash</u> <sup>b</sup>
0.65	0.05	---
0.71	0.05	---
0.81	0.05	---
0.99	0.05	---
1.03	0.09	---
1.10	0.05	0.70
1.16	0.85	---
1.22	0.05	0.70
1.24	0.05	---
1.40	0.78	---
1.51	1.32	---
1.54	1.01	---
1.56	1.12	---
2.04	1.08	---

<sup>a</sup>Values in mg C/ft<sup>2</sup>; multiply by 0.011 to convert to g C/m<sup>2</sup>

<sup>b</sup>Values in mg residue/ft<sup>2</sup>; multiply by 0.011 to convert to g residue/m<sup>2</sup>

TABLE 2

RESULTS OBTAINED FOR SAMPLES OTHER THAN COLD-ROLLED STEEL

Sample	Direct Oxidation <sup>a</sup>	Chloroform Wash <sup>b</sup>
Galvanized Steel	1.12	----
Galvanized Steel	5.55	----
Galvanized Steel	5.94	----
Galvanized Steel	8.02	12.0
Galvanized Steel	8.43	13.0
Galvanized Steel	26.66	----
Galvanized Steel	27.36	----
Galvanized Steel	40.58	46.0
Galvanized Steel	45.77	55.0
Chemically Treated Steel	1.12	----
Chemically Treated Steel	1.78	----
Low Oxidized 600 <sup>o</sup> C	1.61	----
Low Oxidized 600 <sup>o</sup> F <sup>c</sup>	2.76	----
Reduced 1400 <sup>o</sup> F <sup>c</sup>	2.63	----
Reduced 1400 <sup>o</sup> F <sup>c</sup>	4.09	----
Aluminum Coated Steel	3.14	----
Grey Iron	Indeterminant <sup>d</sup>	----
Graphite	Indeterminant <sup>d</sup>	----

<sup>a</sup>Values in mg C/ft<sup>2</sup>; to convert to g C/m<sup>2</sup> multiply by 0.011.

<sup>b</sup>Values in mg residue/ft<sup>2</sup>; to convert to g residue/m<sup>2</sup> multiply by 0.011.

<sup>c</sup>°C = (°F - 32) x 5/9

<sup>d</sup>Values indeterminant because high sample blanks were obtained due to reaction of carbon in the samples.

Table 2 lists values obtained on a number of samples other than cold-rolled steel. HCl swab values are not available because sample are too porous to permit the analysis or are over reactive with HCl. The chloroform wash values for other than cold-rolled steel samples are in reasonable agreement with the direct oxidation values in that they suggest the residue is approximately 65 to 88% carbon, values not unreasonable for organic materials. The actual surface contamination has not been characterized at this time but may also contain elemental carbon which would raise the expected percent carbon in the residue. The 2 values for the chloroform wash method shown in table 1 for cold-rolled steel are lower than expected based on the direct oxidation results but do support the possibility that the HCl swab method yields low results. The chloroform wash may fail to remove materials which are not soluble in chloroform or are tenaciously bonded to the surface.

Grey iron and graphite could not be analyzed by the direct method because carbon contained within them reacted, as indicated by a steady release of CO<sub>2</sub> continuing beyond 20 minutes.

TABLE 3

REPLICATE DIRECT OXIDATION RESULTS FOR TYPICAL SAMPLES OF COLD-ROLLED STEEL

Sample	Results <sup>a</sup>	Mean <sup>a</sup>	Standard Deviation <sup>a</sup>
1	1.55, 1.40, 1.49, 1.61	1.51	0.08
2	0.44, 0.61, 0.92, 0.93, 0.41, 0.57	0.65	0.21
3	1.56, 1.19, 1.29	1.35	0.16
4	1.02, 1.02, 0.85, 1.06	0.99	0.08
5	1.02, 0.99, 1.18, 0.91	1.03	0.10
6	1.03, 1.34, 1.10, 1.48	1.24	0.17

<sup>a</sup>Values in mg C/ft<sup>2</sup>; multiply by 0.011 to convert to g C/m<sup>2</sup>.

Since the graphite was oxidized, it is assumed that similar graphite occurring on the surface of a sample would be oxidized and detected. The author has found that carbon in diesel fuel exhaust particulates is oxidized at 550<sup>o</sup>C. It should be recognized that not all forms of carbon are oxidized at 580<sup>o</sup>C. If a specific type of contaminant is likely to be present tests can be performed to confirm that it is oxidized and detected.

Table 3 shows typical values obtained for replicate determinations on cold-rolled steel samples using the direct oxidation method. The standard deviations, 0.08 to 0.21 mg C/ft<sup>2</sup> (0.0009 to 0.0023 g C/m<sup>2</sup>), suggest that sample homogeneity limits the obtained precision. This limitation may be improved by modifying the combustion tube so that larger samples can be used. A modified combustion tube was not prepared because of the limited number of samples to be evaluated.

Although the equipment does not require the analysis of standards they can be prepared and should be analyzed periodically to confirm proper operation of the equipment. When samples of benzoic acid containing over 1 mg carbon are analyzed using 1000<sup>o</sup>C as the combustion temperature relative accuracy of ±0.3% is obtained. Table 4 lists values obtained by analyz-

TABLE 4

RECOVERY OF CARBON FROM ORGANIC STANDARDS USING 580<sup>o</sup>C OXIDATION

Sample	Theoretical %C	Mean %C Found	Mean % Recovery
Diocetyl Sebacate <sup>a</sup>	73.2	74.4	101.7
Benzoic Acid <sup>b</sup>	68.8	54.4	79.0
Sulfonilamide <sup>b</sup>	41.9	39.7	94.8

<sup>a</sup>Sample coated on cleaned cold-rolled steel.

<sup>b</sup>Sample contained in platinum boat.

ing benzoic acid, sulfonilamide and dioctyl sebacate at 580°C. The low results for the benzoic acid and sulfonilamide indicate they were not completely oxidized. Benzoic acid and dioctyl sebacate discolored the acid dichromate scrubber, a further indication of incomplete oxidation. The incomplete oxidation may be due in part to their high volatility and the low oxidation efficiency of the barium chromate catalyst at 580°C. The optimum temperature for use of barium chromate as an oxidation catalyst is 700 to 800°C. Other catalysts were not tried because of insufficient time. Low temperature oxidation (450°C) was used by Heistand(3) to determine organic carbon in oil shale with satisfactory results. Organic materials in soda ash ( $\text{Na}_2\text{CO}_3$ ) have found to be oxidized at 530°C by the author. Efficient oxidation of most organic materials can be expected if sufficient active catalyst is used. For the samples analyzed no evidence of incomplete oxidation was found. If low recovery is obtained or other evidence of incomplete oxidation exists other catalysts should be used or the apparatus modified so that the barium chromate is used at 700 to 800°C. When low recovery is suspected because of the nature of the contaminant recoveries may be determined using samples of the contaminant as standards. Higher analysis temperatures may be used if the samples do not contain carbon which is also oxidized. Other types of samples which have been analyzed successfully for surface carbon contamination include: particulates collected on glass, quartz and silver filters and organic coatings on inert substrates.

The recovery of dioctyl sebacate was complete, within experimental error, and indicates efficient oxidation can be achieved for organic coatings on metal surfaces. The small amount and thin film of contaminants on samples may help ensure complete oxidation and the metal surface may act as an oxidation catalyst. Because of the mass of the samples their temperature rises less abruptly than standards in platinum boats when they are inserted into the furnace. The resulting slower vaporization may also permit more efficient oxidation of the contaminants.

#### SUMMARY

A method has been developed for quantitative determination of carbon on metal surfaces. Organic materials and some forms of elemental carbon on the metal surface are oxidized in an oxygen atmosphere at a temperature which will not cause carbon within steel to react. The resulting  $\text{CO}_2$  is coulometrically titrated. The analysis is completed in less than 10 minutes and is easily performed without special operator skills. Preparation of standards is not required and the method is applicable to all levels of contamination likely to be encountered. The minimum detection limit is approximately 0.02mg  $\text{C}/\text{ft}^2$  (0.0002g  $\text{C}/\text{m}^2$ ). Although the method has been shown to be appropriate for many samples, some materials such as grey iron cannot be analyzed. Samples that cannot be analyzed because

they contain compositional carbon that is oxidized are easily identified by the continuous release of  $\text{CO}_2$  from them.

Some samples may contain contaminants which are not oxidized under the analysis conditions. For inorganic carbon contaminants further work is needed to determine detection capability. If specific contaminants are suspected of not being detected they can be run as standards and recoveries determined.

Direct oxidation appears to offer a substantial benefit in time savings and increased capability of detection for some contaminants.

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#### ACKNOWLEDGEMENTS

The assistance of Phillip Coduti of Inland Steel Company, East Chicago, Indiana, Joe Claus, 3M Company, St. Paul, Minnesota and Ed Huffman, Jr. of Huffman Laboratories, Inc. is gratefully acknowledged. Phillip Coduti provided all the data reported for the HCl swab and chloroform wash methods.