

Trace Determination of Hydrogen in Coke by Elemental Analysis

Romolo Cicciarelli^{a*}, Basil Zuber^b, and Christian Ambort^a

Abstract: Recarburizers used in the steel industry are ruthlessly selected according to their quality. One of the critical parameters is the residual hydrocarbon content of the coke or graphite-based products. The current analytical procedure has a detection limit of about 0.2% hydrogen. The dynamic flash combustion of the sample coupled with gas chromatography (GC) was used to develop a simple method for the determination of hydrogen traces in coke. The sample was burned in an oxygen/helium atmosphere at 1020 °C. Separation of the combustion gases, NO₂, CO₂, H₂O, and SO₂, is accomplished on a chromatography column and measured by a thermal conductivity detector TCD. A linear response of hydrogen over a concentration range of 98–4910 mg kg⁻¹ with a correlation coefficient of 0.9985 has been achieved. A detection limit of 26 mg kg⁻¹ and a determination limit of 92 mg kg⁻¹ were obtained with new equipment configurations and a sample weight of 8 mg. This corresponds to an impressive improvement of sensitivity of a factor of over 70. The coefficient of variation was found to be 31.3% at a concentration of 98 mg kg⁻¹ and 0.7% at 4910 mg kg⁻¹.

Keywords: Coke and graphite · Elemental analysis · Gas chromatography · Recarburizer · Trace determination of hydrogen

1. Introduction

The determination of carbon, hydrogen, nitrogen, and sulfur is performed typically in the range 0.3–100%. The goal of this work was to reduce the detection limit for hydrogen from 2000 mg kg⁻¹ to 100 mg kg⁻¹.

The detection of hydrogen is usually performed by dynamic flash combustion coupled with gas chromatography (GC). A Porapak QS column is used to separate the combustion gases [1][2]. With this column the separation of the different gases is sufficient for high concentrations, but the main disadvantage is that the peak of hydrogen

presents a broad tailing. This phenomenon is not important for a concentration of several percent but for lower concentrations this tailing is a big problem for the quantitative analysis (Fig. 1). This study explores the use of other GC-column types; optimum results were obtained with a HayeSep D column. The connecting plastic tubes were replaced by stainless steel tubes, resulting in lower blank values.

2. Experimental

2.1. Materials and Reagents

A CHNS-O EA1108 Elemental Analyzer (Carlo Erba Instruments) equipped with an autosampler AS-200 LS (50 pos. drum), a combustion/reduction reactor (CHNS packed reactor art. no 299.0733.10: quartz wool, tungsten anhydride, pure copper wires), a 2 m × 5.2 mm i.d. 80/100 mesh HayeSep D column (art. no 455523, msp Friedli&Co) and a thermoconductivity detector (TCD) were used for the analysis (Fig. 2). The analysis procedure was controlled by Eager 200 software. Samples are

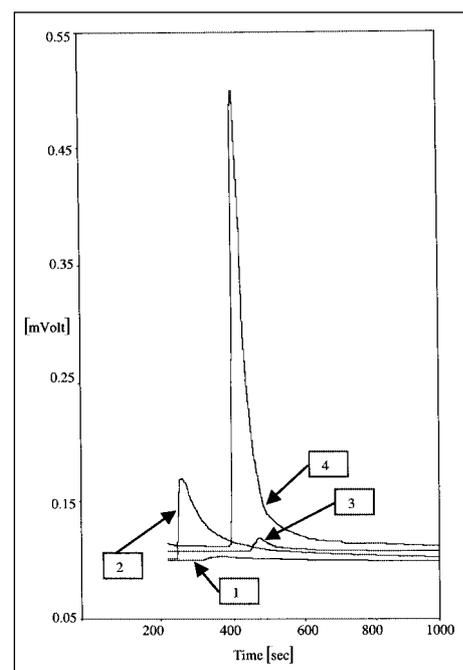


Fig. 1. Comparison of Porapak QS and HayeSep D columns: 1) blank with Porapak QS; 2) standard 4910 mg kg⁻¹ with Porapak QS; 3) blank with HayeSep D; 4) standard 4910 mg kg⁻¹ with HayeSep D.

*Correspondence: Prof. R. Cicciarelli^a
^aUniversity of Applied Sciences of Western Switzerland
Department of Chemistry
CH-1950 Sion 2
Tel.: +41 27 606 86 60
Fax: +41 27 606 85 15
E-Mail: romolo.cicciarelli
^bR&D Carbon Ltd.
P.O. Box
CH-3960 Sierre

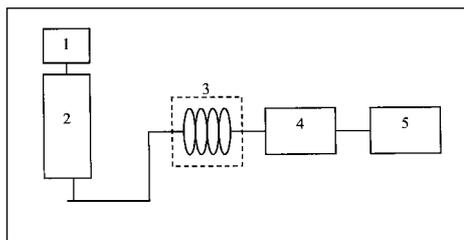


Fig. 2. Schematic layout of the Elemental Analyzer EA1108 with 1) autosampler AS-200 LS; 2) combustion/reduction reactor; 3) GC column; 4) thermoconductivity detector (TCD); 5) data treatment system. All connecting tubes are made of stainless steel.

weighed in tin capsules (Sn 97.5; 0.15 ml content, art. no 176.9811.26) on a microbalance (± 0.01 mg, Mettler Toledo AT250, Switzerland).

The carrier gas was helium 5.0 (purity 99.9990%, PanGas, Switzerland) and oxygen 6.0 (purity 99.99990%, PanGas, Switzerland) was used for combustion. The autosampler was regulated by synthetic air (PanGas, Switzerland) [3].

2.2. Analytical Conditions

Flow [ml/min]	He Meas.	100
	He Ref.	40
	Oxygen	12

Pressure [kPa]	He Meas.	≈ 120
	He Ref.	≈ 20
	Oxygen	≈ 145
	Air autosampler	280

Temperature [°C]	Left (packed reactor)	1020
	Right (no reactor)	650
	Oven (GC) (isotherm)	65
	Filament (Detector)	190

Time [s]	Analytical time	950
Sample Start	12	
Sample Stop	60	
Oxygen Injection Stop	80	
Peak Enable Start	10	

2.3. Analytical Procedure

The sample was weighed on a microbalance in a tin capsule. The weight depends on the type of sample. In this work the weight was 1, 2, 8, and 16 mg (± 0.01 mg), respectively; this step must be carried out very accurately. After weighing

the tin capsule was closed and inserted into the autosampler. The measuring sequence was started.

3. Results and Discussion

3.1. Porapak QS versus HayeSep D Columns

The analysis of traces of hydrogen (100 mg kg^{-1}) is very difficult with the original Porapak QS column. The peak showed a broad tailing (500 s), therefore the integration of the area was very delicate. This gas chromatography column was replaced by a HayeSep D column, with the result that the hydrogen peak was much sharper. The tailing was reduced and the width of the

peak was about 170 s. Fig. 1 shows the difference between these two gas chromatography columns (Porapak QS and HayeSep D). The result of a change in gas chromatography column is an easier and more accurate integration of the peak with a HayeSep D column.

3.2. Calibration Curve and Detection Limit

The sample weight was varied from 1 to 16 mg in order to determine the sample size with the lowest limit of detection (Table 1). The linear calibration curve peak area versus the concentration of the standard graphite using HayeSep D column is shown in Fig. 3.

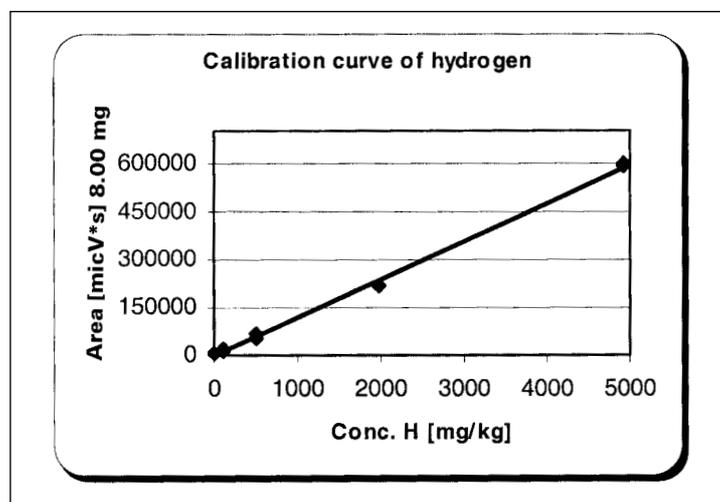


Fig. 3. Calibration curve of hydrogen with HayeSep D (8 mg weight).

Table 1: Features of the calibration graphs and determination of traces of hydrogen with a HayeSep D or Porapak QS column

GC-column type	Weight of standard [mg]	Regression equation ^a	r ^b	LOD [mg/kg] Blank-value-method ^c	Number of analyses for each standard
Porapak QS	1.00	A = 12.7 X + 6668	0.9984	294	2
HayeSep D	2.00	A = 34.1 X + 9069	0.9990	96	3
HayeSep D	8.00	A = 121 X + 2953	0.9985	26	6
HayeSep D	16.00	A = 242 X + 22046	0.9995	22	2

^aA = analyte peak area (micV*s); X = hydrogen concentration (mg/kg).

^br = Correlation coefficient.

^cCalculates the limit of detection (LOD) with the blank-value method (calculation program valida 3.00).

3.3. Determination of Accuracy by Measuring the Calibration Samples as Samples

Standard graphite substances were determined as samples after calibration with standard graphite substance. The hydrogen concentrations are given in Tables 2, 3 and 4.

Table 2. Obtained accuracy by determination with **1mg** samples with the Porapak QS column

Compound	Theoretical conc. [mg/kg]	Mean value [mg/kg]	Deviation ^d	Relative Deviation ^e [%]	No. of samples
Standard 1	98	29	69	70	2
Standard 2	491	400	91	19	2
Standard 3	1964	1808	156	8	2
Standard 4	4910	3771	1139	23	2

^dDeviation = |mean value – theoretical conc. |

^eRelative Deviation = (|mean value – theoretical conc. |) / theoretical conc.

Table 3. Obtained accuracy by determination with **2mg** samples with the HayeSep D column

Compound	Theoretical conc. [mg/kg]	Mean value [mg/kg]	Deviation ^d	Relative Deviation ^e [%]	No. of samples
Standard 1	98	161	63	64	2
Standard 2	491	534	43	9	2
Standard 3	1964	1857	107	5	2
Standard 4	4910	4766	144	3	2

Table 4. Obtained accuracy by determination with **8mg** samples with the HayeSep D column

Compound	Theoretical conc. [mg/kg]	Mean value [mg/kg]	Deviation ^d	Relative Deviation ^e [%]	No. of samples
Standard 1	98	137	39	40	2
Standard 2	491	488	3	1	2
Standard 3	1964	1774	190	10	2
Standard 4	4910	4861	49	1	2

4. Conclusion

Through modification of a few components of the instrument, of the connecting tubes and the separation column, the method for determination of hydrogen in coke has been substantially improved. With a sample weight of 8mg the detection limit has been lowered from 2000 mg kg⁻¹ to 26 mg kg⁻¹.

Received: April 26, 2002

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