

ASTM D7454 VIBRATED BULK DENSITY METHOD – PRINCIPLES AND LIMITATIONS

Francois Laplante and Luc Duchesneau
Rio Tinto Alcan; 1955 Mellon Boulevard; Jonquière, Québec, Canada

Keywords: Vibrated bulk density, VBD, Coke specification

Abstract

This method, proposed by Rio Tinto Alcan and approved by ASTM in 2008, differs from method D4292 by the introduction of a semi-automated equipment and also by referring to a tighter sample preparation procedure. The performance expressed in terms of repeatability is ≤ 0.008 g/mL when the preparation variance is not included and 0.01 g/mL when the preparation variance is included. The intra-laboratory reproducibility over a two-year period came out to 0.02 g/mL. The inter-laboratory reproducibility has not yet been systematically determined but appears to be high, considering the large punctual differences observed between coke providers and coke purchasers. The underlying principles of D7454 will be presented, the factors causing differences between laboratories will be discussed and a mitigation strategy will be proposed.

Introduction

The vibrated bulk density (VBD) is known as an important technique for calcined coke characterization. The VBD value influences the binder control equation, [1] which itself influences the amount of pitch required during the production of prebaked anode [2]. Concurrently, the VBD is used to predict the green apparent density, and to some extent, the baked anode density [2, 3]. In order to achieve good anode quality, the cokes with the highest purity and the highest vibrated bulk densities are wanted.

However, reported coke bulk density is sensitive to sample preparation and the results vary according to the laboratory where the measure is taken. In addition, the degradation of coke quality exacerbates the difficulty to compare results between the coke providers and the coke purchasers. In the past, Rio Tinto Alcan established the minimum specification for coke quality at 0.82 g/cc. Below this value, the coke requires particular attention.

To remedy the situation when coke is close to the lower specification limit, the VBD technique must be improved to optimize the reproducibility value. The apparatus was designed to achieve this objective and was presented for the first time in 1997 by Duchesneau [4]. The main differences of the Alcan method (ASTM D7454) with respect to ASTM D4292 is *i*) the use of a photo detector which stops the analysis at a given volume of coke and *ii*) a tighter sample preparation procedure. Such an approach minimizes the external sources of error and promotes the inter-laboratory reproducibility.

The present paper outlines the performance and the limitation of ASTM method D7454 using information and data extracted from different round robins held at different times over the past ten years and emphasizing the influence of the coke preparation on the VBD measurements.

Experimental

Automated Apparatus for VBD Measurement

The vibrated bulk density semi-automated apparatus (VBD) is presented in Figure 1. The equipment was jointly developed by Rio Tinto Alcan and STAS; a company specializing in the development, fabrication and commercialization of new equipment for aluminum industry. The instrument consists of a control panel, a vibrating bowl, and a graduated cylinder equipped with a photo detector fixed to an electromagnetic jogger. The control panel allows the adjustment of the vibration set point of the electromagnetic jogger and the control of the material flow passing through the vibrating bowl. The complete details surrounding the instrument set-up and calibration, are provided in references [4-6]

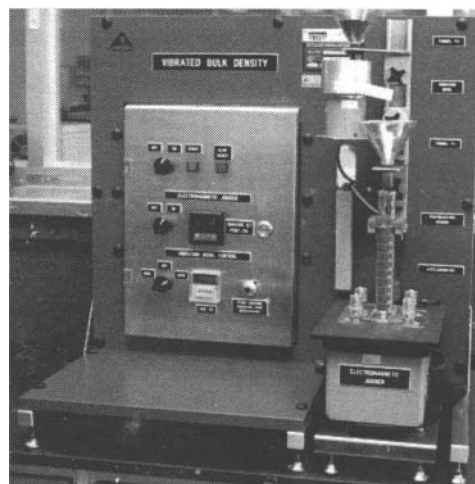


Figure 1: Automated Apparatus for VBD Measurements

Sample Preparation

According to ASTM D7454 method, 1 kg of the natural coke sample was collected and sieved on a -4×14 Tyler mesh sieve. Then, a portion of 180-200 g of -4×14 was collected and further reduced with a roller crusher to -20×35 Tyler mesh. A fraction of 100 g was collected for the VBD measurement.

Sample Analysis

The -20×35 fraction was analyzed with the automated apparatus for the VBD measurement presented in Figure 1. The coke sample was placed in the upper funnel and the VBD apparatus was started. When the coke level reached half of the cylinder level, the apparatus was stopped and the coke remaining in the cylinder

was returned in the upper funnel. The purpose of this procedure was to assure a constant bed in the vibrator bowl.

Once the coke level was uniform in the upper funnel, the chronometer was reset and the analysis was started. The cylinder filling had to be completed in 150 ± 15 sec. When the coke level reached 50 mL, the photo detector stopped the feeding. The cylinder was removed and then weighted to the nearest 0.01 g. For each sample, two additional readings were achieved. The vibrated bulk density was calculated based on average weight of coke over the calibrated volume of the cylinder.

Results and Discussion

Table I shows the results of a survey held in 2001 as part of a round robin organized by ASTM Subcommittee D02.05.0D on Petroleum Coke. This highlights the large diversity in the way the VBD methods were performed by the participating laboratories, despite the fact that many of them reported following the ASTM method D4292. It was obviously not surprising to observe differences between the results obtained.

The ASTM committee had since tried to find a way to obtain a better conformance to the stated analytical parameters. RTA then proposed its method, which appeared to be a bit more directive and offered the advantage of a semi-automated measurement. Discussions and evaluation lasted for many years until, in 2008, RTA method was finally approved as ASTM method D7454.

The performance of the method, evaluated and expressed as the instrumental repeatability (a 10×35 mesh prepared portion analyzed 12 times in a very short period of time), the whole analytical repeatability (8 representative original portion of a same coke prepared and analyzed within one working day) and the intra-laboratory reproducibility (drift standard analyzed over a three-year period), are summarized in Table II.

Table II: Performance of ASTM D7454 Method to Determine VBD

Method	Instrumental Repeatability (g/cc)	Repeatability (g/cc)	Reproducibility (g/cc)
7454	0.008	0.012	0.020
4292 [7]	-	0.014	0.046

The inter-laboratory reproducibility has not yet been systematically determined, the ASTM method D7454 has not yet been implemented in many laboratories external to RTA. However, punctual inter-laboratory comparisons held in the recent past years permitted to appreciate the achievable agreement.

In 2007, an inter-laboratory comparison, involving four laboratories and three samples, showed (Figure 2) a large scattering in the results.

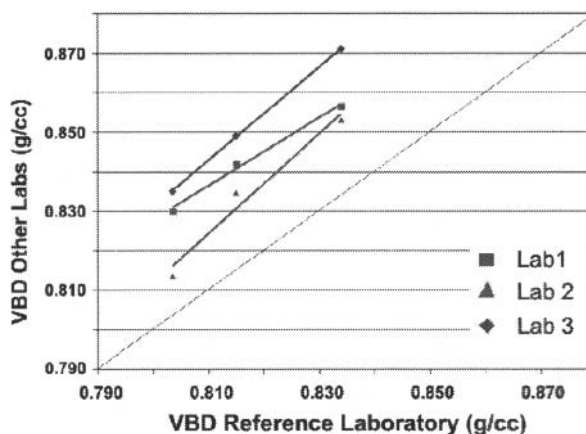


Figure 2: Influence of the sample preparation method during VBD measurement (2007 Mini-Round Robin Results)

In an attempt to establish the cause of this scattering, all the prepared portions were sent to the reference laboratory to be analyzed by the same instrument and thus allow comparison between the laboratories for prepared samples. Figure 3 shows that the results grew closer when the variance coming from the preparation was taken out, indicating at the same time that the difference between the results is mainly due to the preparation step.

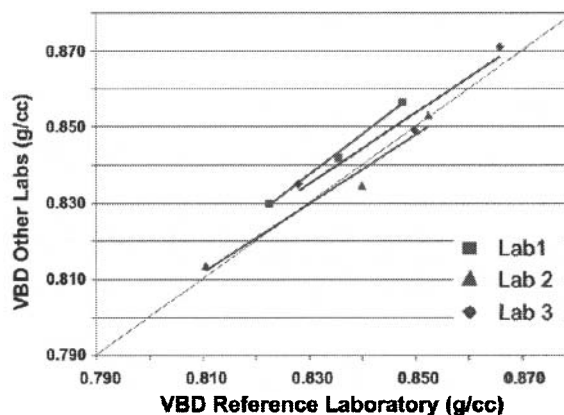


Figure 3: Samples analysis from three labs for a unique preparation made by the reference laboratory (2007 VBD Mini-Round Robin Results)

To investigate the impact of the preparation step, particle size distribution of all 20×35 portions, prepared by each laboratory and used to get the results showed in Figure 2, was determined using Ro-Tap¹ technology. The results presented in Figure 4 show good reproducibility of the preparation process within the laboratories.

¹ Ro-Tap is a registered trademark of Haver Tyler, Inc

Table I: 2001 Survey of experimental conditions used for VBD Measurement

Lab	Instrumental Setup			Sample Preparation				
	Preparation	Sieving	Analytical portion	graduated cylinder	calibration	cylinder filling	Vibrating device	Vibration monitoring
Original ASTM D4292	original crushed to 28 X 48 mesh (prebaked)	grind 2 Kg Jaw crusher; Gap 5 mm	grind 28 X 48 roller crusher; steps depends size factor (start with 28 X 48 mesh)	250 mL	yes; water	funnel; 70-100 sec	Syntron jogger calibrated 0.20-0.22 mm (peak) at 60 Hz	
Lab A-1	original crushed to 28 X 48 mesh	grind 600 g Jaw crusher; gap 1.5 mm (4 mesh)	grind 28 X 48 roller crusher; gap 1.5 mm	250 mL	yes; water	vibrating spatula; 90 +/- 15 sec	Syntron jogger calibrated 0.20 mm (peak) 90 sec during filling	Yes
Lab A-2	original crushed to 28 X 48 mesh	grind 300-500 g Jaw crusher; to <0.25 inch	grind 28 X 48 roller crusher; 2 steps	150 mL	yes; water	Laborette 24; 90 sec	Syntron jogger calibrated 0.20-0.22 mm (peak) 90 sec during filling	Yes
Lab B	extraction of 2.8 x 1.4 mm			1000 mL; steel		manually	graphite load screening machine 30 min	
Lab C	extraction of 28 X 48 mesh			250 mL		manually; 60-90 sec	Syntron jogger calibrated 0.20-0.22 mm (peak) at 60 Hz; 5 min	
Lab D-1	original crushed to 28 X 48 mesh	grind 750 g Chipmunk; gap 1.5 mm (4 mesh)	grind 28 X 48 roller crusher	250 mL	yes; water	vibrating spatula; 70-110 sec	Syntron jogger calibrated 4 min	yes
Lab D-2	original crushed to 28 X 48 mesh	grind 28 X 48 roller crusher; gap progressively decreased	grind 28 X 48 roller crusher; gap progressively decreased	250 mL	yes; water	manually during filling	Syntron jogger calibrated 5.7 Mils	
Lab E-1	original crushed to 28 X 48 mesh	grind 1 pint Jaw crusher	grind 28 X 48 roller crusher; gap progressively decreased	250 mL	yes; water	funnel; >90 sec	Syntron jogger calibrated looking for plateau ... 5 min	
Lab E-2	original crushed to 28 X 48 mesh	grind 600 g cone crusher	grind 28 X 48 roller crusher; gap progressively decreased	150 mL	yes; water	vibrating spatula; 10 mL/30 sec	Syntron jogger calibrated 0.37-0.3877 5 min	yes
Lab F	original crushed to 28 X 48 mesh	750 g	grind 28 X 48 roller crusher; gap progressively decreased (0.25, 0.07, 0.02 inch)	250 mL	certified calib.	modified 500 mL buret 85-100 sec	Syntron jogger calibrated 0.20-0.22 mm 5 min	
Lab G	extraction of 4 X 14 mesh; grinding to 20 X 35 mesh	Original portion 1 Kg Extract 4X14 (approx 200g)	grind 20 X 35 roller crusher; gap progressively decreased (4, 1.5, 1.0, 0.5 mm)	amount to fill 50 mL	yes; water	vibrating bowl	Syntron jogger calibrated with standards 150 sec during filling	yes

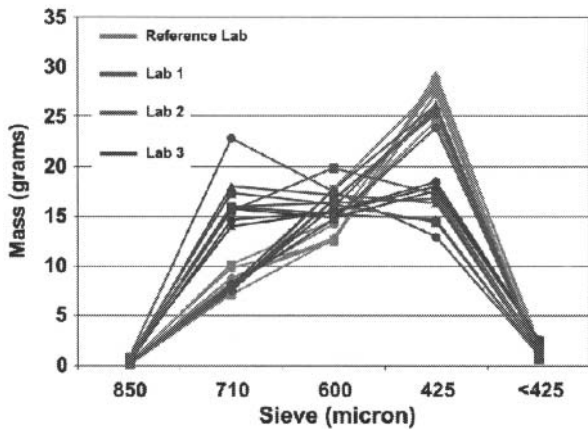


Figure 4: Particle Size Distribution of all the 20 x 35 Mesh Portions of the 2007 Mini-Round Robin

Differences in particles size distribution pattern from one laboratory to the other cannot be correlated to the difference among VBD results.. One hypothesis to explain the variations observed at figure 2 is that for a given particle size distribution, the particle shape is likely the principal source of variations. However, this aspect was not investigated in the present paper.

Many technical exchanges and discussions took place between the laboratories involved. Among the improvement resulting from this inter-laboratory collaboration, the sample preparation was improved. The feeding speed through the roller crusher was modified, the gap between the rolls was adjusted more precisely and the sieving time required preparing the sample before the final analysis was framed. This ensured that each lab was performing the method the same way, thus permitting to improve agreement between laboratories and getting closer to the expected relationship (dotted line in Figure 5). Framing the preparation step had a beneficial effect on VBD measurement as confirmed by the results (Figure 5) obtained by each laboratory during a round robin in 2009. The round robin involved 14 laboratories, two different samples (low and high VBD) and different methods. The graph presents the 2007 results (bold bullets) and shows the improved results from the round robin performed in 2009 (clear bullets).

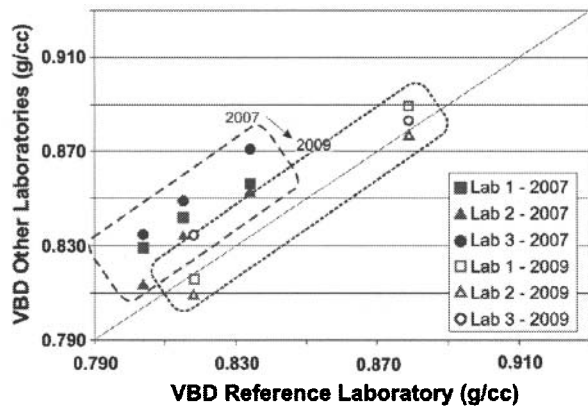


Figure 5: 2007 and 2009 Round Robin Results

During the round robin in 2009, the coke samples were analyzed by 14 laboratories. Among those labs, they were RTA labs and other laboratories. The bulk density was measured according to the technology available in each participant laboratory. Among all the technique used, several laboratories were performing bulk density measurement using the ASTM D4292 method and others were using the ISO 10236 method. Inside RTA, the D7454 method was preferred but two laboratories are still using a modified protocol for the D7454 and one laboratory is using the old Alcan 883 method [4]. The overall results of the 2009 round robin are gathered in Figures 6 and 7. Each graph shows two bullets, indicating that each sample was analyzed in duplicate. The results obtained by each of the laboratories grouped as per the method being applied; thus permitting to appreciate within and between laboratories, as well as within and between methods performance. The error bar for each point represents the intra-laboratory reproducibility standard deviation (Table II).

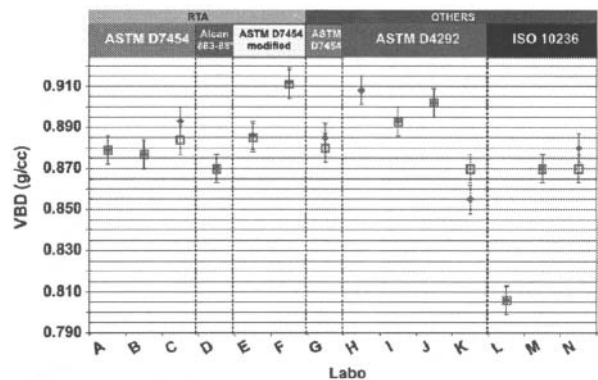


Figure 6: 2009 RTA Round Robin Results – Sample A

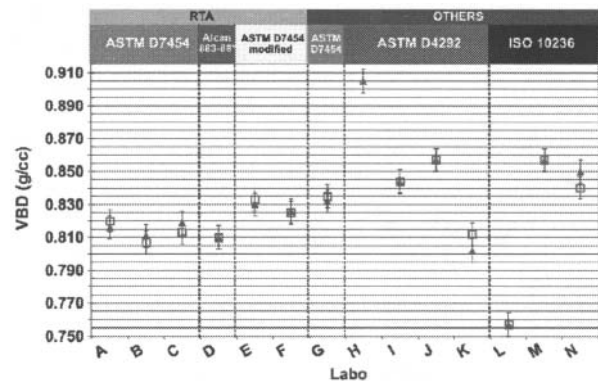


Figure 7: RTA Round Robin Results – Sample B

The figures 6 and 7 are showing a low variation when the ASTM D7454 method is performed in accordance to the written procedure. However, a modification to the operational procedure leads to an increase of the results range. This trend was observed with the modified D7454 method. In such a case, a lack of crusher or a different coke fraction is responsible for results deviations. The variations observed by the laboratory which performed the D4292 are induced by the latitude offered by the method. In fact, there is no sieving range imposed with the D4292 and the ISO 10236 and since the method of sample preparation

can affect the packing characteristics due to differences in the particle shapes, the variation observed with the ASTM D4292 and the ISO 10236 were expected.

Despite the fact that those round robin results cannot be compared on a statistical basis, they permit to state that ASTM method D7454 performance is at least comparable, if not better, to the other standard method. On the other hand, there is room and need for improvement in the new context where, because of the decreasing quality of coke quality, the VBD of the available coke becomes closer and closer to the minimum specification.

Conclusion

Performance improvement of the method is directly linked to the refinement and tighter control of preparation process. Further investigation has been initiated to better identify and understand the factors impacting the quality of the preparation such as the particle size distribution, particle shape, and roller design, including the spacing between the rollers, the roller feeding rate and others with the desire to preserve the results historic. Other mid-term, long-term options are also being considered such as elimination of grinding, exploring other types of grinding, or the use of 3D image analysis.

References

1. A.L.Proulx. Light Metals 657 (1993).
2. D.Belitskus. Light Metals 863 (1974).
3. D.Belitskus and D.J.Danka. Light Metals 429 (1989).
4. L.Duchesneau, R.Lessard, A.Gendron, and G.Brassard. Light Metals 497 (1997).
5. STAS Inc. Vibrated Bulk Density Device (VBDD). 2009.
6. ASTM. Standard test method for determination of Vibrated Bulk Density of Calcined Petroleum Coke using a Semi-Automated Apparatus. ASTM method D7454, 2008.
7. ASTM. Standard Test Method for Determination of Vibrated Bulk Density of Calcined Petroleum Coke, ASTM method D4292, 2010