

Determination and Detection of Possible Carbon Black Fugitive Emissions

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INTRODUCTION

Carbon Black is a fine black powder that has been manufactured commercially for many years. It is a simple fact that whenever a black colored environmental contamination is observed near a facility that produces or uses this fine black powder then the immediate suspect is carbon black. However, black colored environmental contaminations are found throughout the world at locations totally remote from carbon black producing or carbon black using facilities, i.e., there are many origins for these contaminations ranging from black mold to diesel soots to soots from burning, etc. Therefore it is clear that good scientific methods are needed to distinguish carbon black from other environmental particulate. It is worthwhile to already state that carbon black is made from hydrocarbons under very controlled conditions and is quite different from the various soots which are made by uncontrolled processes.

For many years the analysis of a black colored environmental contamination (in order to determine origin) was left up to an analyst's discretion and many methods were claimed to be able to identify carbon black in such a contamination, oftentimes without scientific evidence that these methods were satisfactory for such purposes. In the early 1990's the North American Product Safety and Regulatory Committee (NAPSRC), which is composed of members from the different carbon black manufacturers and scientific consultants, saw the need for a standard practice for analyzing these samples. Only in this way could there be the formation of an agreement on the best scientific methods to employ for testing these type of samples. The task of developing this standard was given to ASTM Subcommittee D24.81 (Microscopy and Morphology of Carbon Black). By taking this approach, the best experts were brought together in a D24.81 task group to develop such a standard practice. This standard development process has been ongoing for several years and appears to be nearing its completion. A standard practice which has undergone many iterations is on the Fall 2000 ASTM D24 Committee Ballot and should be approved by December 2000. It is the purpose of this paper to describe this standard and help the potential users understand the usefulness as well as the limitations of this standard

DISCUSSION

The standard practice that has been developed is intended to describe the procedures and protocols to follow in order to collect possible fugitive emission/environmental samples and determine whether these samples contain materials which are consistent with the composition and morphology of carbon black. First, the procedure provides specific guidelines for the critical step of proper sampling and handling of these samples. The primary section of this standard practice then describes the analysis of the sample(s)

using Transmission Electron Microscopy (TEM). This method is the most critical in determining if the collected sample is consistent or inconsistent with the unique morphology of carbon black which can only be observed at the high magnification this technique provides. Use of the TEM method is mandatory in applying this standard. The standard also describes additional ancillary techniques that may or may not be included in a sample analysis for purposes of providing supporting information as to the nature of the sample material. One of the most important uses for the ancillary techniques is to distinguish soot from carbon black. Each case may warrant some, none, or all of the ancillary techniques depending on the situation and whether the technique can possibly provide critical identification information.

One of the most difficult aspects in most cases of suspected carbon black fugitive emissions is the small amount of material that can be sampled and used subsequently for analysis. This makes the sampling step quite critical. Samples are to be collected by two primary techniques, one with sticky tape and the other with either polyester balls or glass fiber filter pads. Precautions are to be taken to carefully collect, handle, and transport samples in a manner to not cause further contamination. At the time of sample collection, a sampling and meteorology record and also a chain of custody record are to be completed. This standard does not preclude examination of samples collected by other means than the above, such as polyethylene glove wipes, filter paper, and samples of clothing or large samples taken in other containers at a spill site, however these factors must be considered in interpretation of the data. In all cases the samples always require thorough identification taken at the time of sample collection.

Although not mandatory, a simple streak test may be performed at the time of sample collection which may give an indication of the presence of newly deposited carbon blacks, soots, or other naturally occurring environmental particulate. In the test, a lens tissue (that has been wrapped around an elongated roll of polyester or cotton balls) is wiped across about a 1-foot length of surface in a continuous motion and observed for streaking. Fresh carbon black and soots will leave a streak on the tissue. Please note that a positive streak test does not identify the material as carbon black since soots and other particulate material also give a positive streak test.

One of the first examinations that may be done is examination under a light microscope although again not mandatory. This technique is only a screening method for an overview of the bulk composition. It can never be used to positively identify carbon black because the maximum magnifications (approximately 1000X with oil immersion) are insufficient to obtain the resolution needed to observe the morphology of carbon black or soot which are nanoparticles. This technique in the hands of a trained specialist can be useful to identify other components (non carbon black or soot) that may be in the sample, such as molds, fungi, pollen fibers, ash, etc. that are large enough to either be resolved by the magnifications possible or identified through techniques such as the use of polarized light.

The transmission electron microscopy (TEM) method is an evaluation of the morphology of the particles present in the sample to determine primarily if their morphology is consistent with the unique grape cluster, or acinoform, morphology of carbon black and some soots and thus this is the one mandatory technique for applying this standard. (See Figure 1) Transmission electron microscopy provides the magnifications required to obtain the necessary resolution to observe the morphology. The composition present in the sample containing acinoform morphology may be estimated from this examination by applying a quantitative approach detailed in an ancillary technique, but this is optional. If no particulates present have the acinoform morphology, it can be concluded that the sample does not contain carbon black. Numerous photomicrographs of carbon blacks, soots, and other materials are provided in the standard to assist the user. A positive test (acinoform morphology) does not identify the particulate as carbon black but indicates that ancillary methods should be used to help distinguish the sample from soot.

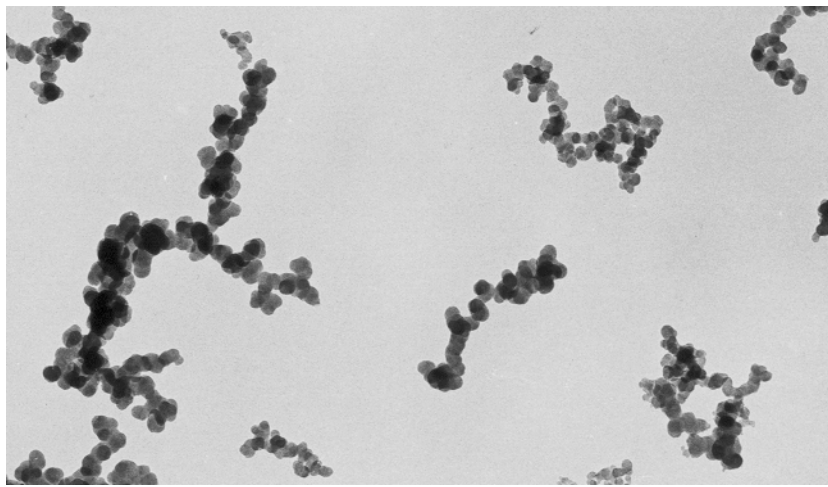


Figure 1: Typical Acinoform Morphology of Carbon Black and some Soots as observed by Transmission Electron Microscopy.

It is worthwhile at this point to discuss in more detail the similarities and difference between carbon black and soot. Carbon blacks are produced commercially by either partial combustion or thermal decomposition of hydrocarbons under controlled conditions (1). Soot, on the other hand, is the unwanted by-product from incomplete combustion or pyrolysis of carbon containing materials (2). Numerous studies have pointed to the differences between these two materials (3-7). Some of the most significant differences are amount of acinoform carbon (>99% in carbon black, quite variable in soot from less than 60% to greater than 95%), sulfur content (0-2% in carbon black based on feedstock but quite consistent, quite variable in soot) and volatile content (fairly low in carbon black, highly variable in soot from very little to greater than 20%). There are many other differences, but because of the limited sample sizes, many are impractical for being useful in distinguishing the two materials.

Thus ancillary methods are also available in the proposed standard to help distinguish whether a sample that was consistent with carbon black under the TEM is or is not consistent with carbon black by other techniques. These ancillary methods include X-ray analysis for composition and thermogravimetric analysis for volatile content. The X-ray method is a semi-quantitative measure of the sulfur content in individual components suspected to be carbon black by energy or wavelength dispersive spectrometry to determine if an individual component in the sample has an appropriate sulfur content consistent with commercially produced carbon black. Controls of locally produced carbon blacks can be very useful. Carbon blacks contain about 97-99.5% carbon and sulfur content ranges from 0% in thermal and acetylene blacks to 0.5-2% sulfur in typical furnace grade carbon blacks. The % sulfur in a carbon black is highly dependent on the % sulfur in the feedstock oil and this should be taken into consideration. Soots, depending on their source may contain greater than 2% sulfur, which distinguishes them from carbon black. However, some soots may contain <2% sulfur, which can make them more difficult to distinguish from carbon black. In addition, this method allows other non-carbon components besides sulfur to be identified which, if present, may constitute the basis for the sample to be inconsistent with carbon black. While this method can demonstrate a sample to be consistent with carbon black it cannot eliminate the possibility that a soot is present with similar properties which is quite possible.

Another ancillary technique, as mentioned above, is a quantitative measure of the volatile organic content of carbon samples by use of thermogravimetric techniques. The method is based on the fact that volatile organics can be removed at high temperatures in an inert atmosphere (e.g., nitrogen) without damage to the carbon black and then by repeating the analysis in air (which then combusts the carbon) the amount of carbon present can be determined. This method can only be applied to samples confirmed by electron microscopy to be primarily aciniform carbon (95%) or samples where the volatile content of the components other than carbon are known or can be accounted for. This method allows the distinction between the types of particulate carbon to be determined as carbon blacks are quite low in volatile organic content (<8%) whereas soots are generally much higher (>20%). Test samples collected on glass fiber pads are heated in nitrogen to 550°C to determine the volatile organic content and then heated in air to 650° to determine the mass of particulate carbon in order to calculate the % volatiles in the particulate carbon. While this technique can distinguish certain soots that have high volatile content it does not help to distinguish between carbon black and a low volatile soot.

An important aspect in using any of these techniques is to consider all factors where information is available as well as simply the results from a test. For example, what type of feedstock is being used to produce carbon blacks in proximity to the contamination and how does that affect for example sulfur content. Whenever possible controls of the suspected carbon black should be tested alongside the sample. This (use of a control) can also apply to any other material besides carbon black that is suspected in a particular contamination.

An ASTM D24.81 Round Robin was conducted in 1998 using this proposed standard with six “blind” samples. Two were carbon black, and the other were a black mold, fireplace soot, diesel soot, and automotive soot. Five laboratories participated and three identified all samples correctly. The other two laboratories identified all the samples correctly except the diesel soot and automotive soot; however, the reasons for their misidentification had known causes and wording was placed in the procedure to prevent future errors of the same type. Another round robin was conducted in 1999 using samples that were not pure samples as in the first study but were more “real world” samples that contained mixtures of many components. This was done to check the robustness of the procedure and find other areas that need improvement. This was also quite successful with the participating laboratories basically all in agreement in regard to observations and interpretation.

CONCLUSION

A standard has been developed that is designed to help clarify what techniques should be used to examine particulate emission samples when the material is suspected to contain carbon black. It cannot address all situations or completely clarify all positions of interpretation of the data, however it can serve the useful purpose of making clear what the standard practice should be in order to collect and analyze these samples. One point that needs to be made clear is although every technique could show a sample to be consistent with carbon black, it cannot eliminate the possibility that the sample contains a soot because not all soots differ from carbon black in the techniques applied in the standard. In most other cases, the techniques set forth in the standard are quite useful for the determination of whether samples are consistent or inconsistent with carbon black

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