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Assay of carbon nanoparticles in liquids

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HIGHLIGHTS

- Carbon black nanoparticles in-situ assay was proposed in 2 types of "green" liquids.
- 1-Butyl-3-methyl imidazolium based ionic liquids and glycerol were studied.
- The changes in the red counts of the RGB image is proportional to the concentration.
- The 2 modes of fluorescence were used for a direct/indirect concentration evaluation.
- We propose to apply the conductivity measurements at high CB concentration.

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ABSTRACT

The critical assay of carbon black concentration suffers from the lack of available methods, especially in-situ methods suitable for nanoparticles. We propose a useful tool for monitoring carbon nanoparticles concentration in liquids by means of RGB imaging, fluorescence and conductivity measurements. In this study carbon black particles of 25–75 nm size were dispersed within two types of "green" liquids (1-butyl-3-methyl imidazolium based ionic liquids and glycerol) and the effect of carbon nanoparticles concentration on the liquids properties was measured. The conductivity of all the liquids increased with carbon concentration, while the slope of the curve was liquid dependent. The fluorescence intensity of ionic liquids decreased dramatically even when a small amount of carbon was added, while water-containing ionic liquids had a more moderate behavior. Glycerol has no native fluorescence, therefore, a known tracer present in soot (dibenzothiophene), having a characteristic fluorescence monitored by synchronous scan mode, was used. The carbon black effect on RGB imaging shows a linear dependence, while the red counts decreases with contamination. The proposed methods are simple and low-cost but nonetheless sensitive.

1. Introduction

Soot is an airborne environmental contaminant resulting from the incomplete combustion of carbon based fuels such as wood, coal, diesel oil or other materials. Size distribution of soot particles covers a wide range from 0.0002 to 500 μm [1]. The initial chemical composition of soot particles depends strongly on its sources: some sources can produce almost pure elemental carbon, while others produce particles of which 50% by mass is organic matter [2]. One of the main anthropogenic sources of atmospheric soot in urban areas are mobile sources, especially diesel engines. The International Agency for Research on Cancer upgraded the carcinogenicity of diesel exhaust to Group 1 (known human carcinogen) in 2012 [3].

Therefore, the diesel particulate matter (DPM) removal techniques are required to reduce the environmental pollution. One of more effective and expedient approaches for DPM removal is based on a scrubber containing suitable absorbent liquids due to its low equipment and maintenance costs combined with operational safety and high collection efficiency [4]. For example, the DPM mass concentration was reduced from 0.013 to 0.027 g/m^3 in an untreated diesel exhaust gas to under 0.002 g/m^3 using such scrubber [4].

A number of chemicals can be employed as absorbents in an aqueous medium in various wet scrubbing. Promising compounds used in scrubbers for CO_2 [5–7] and SO_2 [5,8,9] absorption are ionic liquids (ILs). ILs are salts with low melting points (below 100 °C), which have unique properties such as wide liquid temperature range, thermal stability, high conductivity, non-flammability

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and adjustable hydrophobicity and polarity [5]. Because the ILs are non-volatile, they do not contaminate the gas stream during gas separation. Imidazolium-based ILs selectively dissolve CO_2, ethylene and ethane have medium solubility, while methane, argon, oxygen, hydrogen, nitrogen, CO has low solubility [10]. Imidazolium-based ILs were reported as an effective dispersant for carbon nanotubes, as well [11].

Based on these characteristics of ILs, we regard them as an optimal absorbent for carbon nanoparticles. In this study we dealt with laboratory scale system for absorbing nano- carbon black by "green" liquids (imidazolium-based ILs and glycerol). "Carbon black (CB) is a quasi-graphitic form of nearly pure elemental carbon that is distinguished by its very low quantities of extractable organic compounds and total inorganics (generally <1% of each). CB has a characteristic particle morphology that consists of aciniform (grape-like) aggregates of highly fused spherical primary particles, with the aggregates clustered into larger-sized agglomerates. It is manufactured by either partial combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions"[3]. CB is in the top 50 industrial chemicals manufactured worldwide, based on annual tonnage (more than 10 million tons) [12]. The International Agency for Research on Cancer evaluated at 2010 CB as Group 2B possible human carcinogen [13]. The greatest potential for CB exposure is during its manufacturing, production, collection and handling and also occur to workers in down-stream used industries [3]. Modern carbon black plants generally emit less than 50 mg/m^3 of CB [13]. The occupational exposure limits and guidelines for carbon black vary in different countries from 2 to 4 mg/m^3 [13].

In this paper, we studied the analytical platform for monitoring pure nano-carbon in liquids, demonstrating the feasibility of the concept. This concept may have further industrial application in areas where monitoring of carbon nanoparticles is relevant: carbon black manufacturing, production, collection and handling and diesel soot removal. Using of commercial CB as a representative analog for diesel soot is based on previously published practice [14–16]. M. Ozawa et al. mentioned that "essentially carbon blacks are the pure soot" [12]. For instance, the overview of characterization of physical and chemical properties of soot by the main off-line analytical techniques reports commercial carbon black (Prinex-U) as a case study [17]. In this context CB in our study is used as a simulation of pure soot. According to Long et al. [3], ambient carbon particles even from the same source can vary hugely by their morphology and chemical composition. For example, diesel exhaust emissions can contain, based on different estimations, 33–90% elemental carbon, when the potential total polycyclic aromatic hydrocarbons (PAHs) content can be found in wide range (85–10000 mg/kg). In this situation, dealing with real atmospheric carbon particles, the analytical methods applied for their characterization could result in a complicated non-producible picture and main effects we seek would be indistinguishable. Therefore, the future industrial application would require a scale-up, taking into account the effects of real atmospheric pollutants that may be present in soot.

Today, several techniques are used for appraisal of the carbonaceous aerosol particles concentration. Real-time evaluation of mass concentration can be performed using optical methods which measure the absorption of light through a filter containing airborne particles (the most widely used method is aethalometry). However, these methods require calibration, may have biases due to liquid-like organics spreading across filter fiber and are sensitive to the relative humidity, pressure and temperature fluctuation [18,19]. Off-line *thermal* and *thermal optical analyses* are measuring carbonaceous particles concentration on a filter or aluminum substrate. The samples are heated stepwise in an oxidizing (or an inert) atmosphere, the filter is illuminated with a laser and the amount of transmitted or reflected light is measured. The principle of this technique and its implementation are straightforward, but the method entails a filter as a substrate collection media and a lengthy collection time (hours). Furthermore, there are different interferences which results in high uncertainty (±20–50%) [18].

There is a lack of available methods and instruments for real time assay of carbon nanoparticles in liquid. A desirable monitoring method for the process control should allow on-line measurements of CB concentration (particularly of nanometric size) in liquids used as an absorbent in scrubbers. Therefore, developing of suitable techniques is a critical matter and presents an analytical challenge, especially in unique absorbent medium such as ionic liquids.

It is known that specific PAHs have been identified as markers of automotive emissions, industrial emissions and crude oils [20]. PAHs are a wide category that includes different groups of compounds, one of which are the thia-arenes, polycyclic aromatic hydrocarbons compounds that contain a thiophene ring [20]. The thia-arenes are used as a tracer in environment pollution investigations and they are known as mutagenic and carcinogenic compounds [21,22]. It was reported that benzothiophene (BT), dibenzothiophene (DBT) and their alkylated homologues are the most abundant organosulfur compounds in diesel fuels [23].

Moreover, it was shown that samples with higher total PAH concentrations tend to have higher concentration of dibenzothiophene isomers [20]. The DBT average concentration in the reference standards of diesel particulate matter is around 10 $\mu g\,g^{-1}$ [SRM 1650b], in coal tar around 20 $\mu g\,g^{-1}$ [SRM 1597] and in urban dust around 0.2 $\mu g\,g^{-1}$ [SRM 1649]. They have fluorescence properties in the solid state [22] and in the solutions (for example, in *n*-heptane) [24–26].

In this work, we propose a novel concept where three well known, sensitive and compelling methods are applied for on line assay of nano-CB concentration in liquids. Preferably, the CB concentration in liquids could be measured using a medium resolution digital photography by means of RGB image, based on the changes in the red counts. Two additional powerful methods capable for nanoparticles concentration measurement are based on fluorescence and conductivity. The fluorescence can be used in a normal scan mode for a direct evaluation of CB concentration or in a synchronous mode scan for an indirect CB concentration evaluation through a tracer (DBT) monitoring. We propose to apply the conductivity measurements for high CB concentrations.

These are extremely simple, low cost methods, which allow for in-situ evaluation of particles concentration. They are practical for the CB monitoring in glycerol and ILs based on 1-butyl-3-methylimidazolium ($Bmim^+$) cation with different anions (Cl^-, Br^-, F^-, PF_6^- and BF_4^-).

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazolium tetrafluoroborate (bmim-BF_4) was purchased from Sigma–Aldrich and was used without purification. 1-Butyl-3-methylimidazolium chloride (bmim-Cl), 1-butyl-3-methylimidazolium bromide (bmim-Br) and 1-butyl-3-methylimidazolium hexafluorophosphate (bmim-PF_6) were synthesized according to known procedure [27]. Mixtures of bmim-Cl and bmim-Br with water were prepared by adding a defined amount of deionized water to the melted (at 80 °C) salt and stirring it to produce the final products contains 3.2 %wt, 4.4 %wt and 10 %wt of water, respectively. 1-Butyl-3-methylimidazolium fluoride (bmim-F) was synthesized according to the procedure proposed in our laboratory [8]. Glycerol (AR, ≥99.5%) was purchased from Gadot, *n*-heptane (AR, ≥98.0%) from Bio-Lab, potassium flu-