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## Arsenic removal from water using flame-synthesized iron oxide nanoparticles with variable oxidation states

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### Abstract

We utilized gas-phase diffusion flame synthesis, which has potential for large-scale production of metal oxide nanoparticles, to produce iron oxide nanoparticles (IONPs) with variable oxidation states. The efficacy of these materials in removal of arsenate (As(V)) from water was assessed. Two different flame configurations, a diffusion flame (DF) and an inverse diffusion flame (IDF), were employed to synthesize six different IONPs by controlling flame conditions. The IONPs produced in the IDF configuration (IDF-IONPs) had smaller particle diameters (4.8 – 8.2 nm) and larger surface areas (141–213 m<sup>2</sup>/g) than the IONPs produced in the DF configuration (29 nm, 36 m<sup>2</sup>/g), which resulted in their higher adsorption capacities. As(V) adsorption capacities of the IDF-IONPs increased when the IONPs were synthesized in more oxidizing conditions. The fully oxidized IDF-IONPs, maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), showed the highest As(V) adsorption capacity, comparable to that of magnetite nanocrystals synthesized by thermal decomposition of iron pentacarbonyl and equivalent to three to four times higher capacity than that of a commonly used goethite-based adsorbent. All IONPs were magnetically responsive, which is of great importance for solid–liquid separation. This study demonstrates that the IONPs synthesized in gas-phase flame, particularly IDF-IONPs, are excellent adsorbents because of their high As(V) sorption capacity, potential for large-scale production, and useful magnetic property.

### Introduction

Arsenic in drinking water poses a significant health risk to human beings across the globe (Nordstrom 2002; Smedley and Kinniburgh 2002). Because of the human health risk (Chen et al. 1988; Smith et al. 2002), the US EPA lowered the maximum contaminant level (MCL) for arsenic in drinking water from 50  $\mu$ g/L to 10  $\mu$ g/L as As in 2002; compliance with the MCL has been required since 2006 (USEPA 2010). Adsorption has been recognized as a promising technique for removing arsenic from drinking water due to its high removal capacity and ease of operation. However, the relatively high cost of adsorbents with high capacity for arsenic has resulted in high treatment costs, particularly for small water systems (Colby et al. 2010). Oxides such as iron oxide can adsorb arsenic – it is known that adsorption on oxides significantly affects the fate and transport of arsenic in the subsurface (Welch et al. 2003). To take advantage of their high adsorptivity, various metal oxide based adsorbents have been deployed in water treatment systems to remove arsenic (Seigal et al. 2007).

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Since metal oxide nanoparticles often exhibit remarkable adsorption capacities compared to their bulk materials (Mayo et al. 2007; Waychunas et al. 2005), various types of nanostructured metal oxide adsorbents have been developed (Chandra et al. 2010; Hristovski et al. 2008; Yavuz et al. 2006). Cost-effective arsenic removal demands the production of adsorbents (e.g., nanoparticles) that have high adsorption capacities using low cost manufacturing methods. Magnetic adsorbents such as magnetite ( $\text{Fe}_3\text{O}_4$ ) nanocrystals (Liu et al. 2008; Mayo et al. 2007; Yavuz et al. 2006), and thiol-functionalized super-paramagnetic nanoparticles (Yantasee et al. 2007) are particularly attractive because of their potential to facilitate solid-liquid separation.

A variety of solution/precipitation techniques have been commonly used to synthesize different types of iron oxides (Cornell and Schwertmann 2003). However, these methods usually utilize a batch process and scale-up may not be straightforward. (Pratsinis 1998). Several aerosol synthesis methods have also been used to produce iron oxides by decomposing iron precursors such as iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) in a furnace (Cabanas et al. 1993; Langlet et al. 1986). In contrast, gas-phase flame synthesis is an attractive method for large-scale production of various materials including nanoscale metal oxides (Pratsinis 1998; Wooldridge 1998). Many oxides such as fumed silica, black carbon and alumina have been produced using the method at rates of approximately millions of tons/year (Pratsinis 1998; Stark and Pratsinis 2002). The flame synthesis methods also enable the design of exotic materials such as carbon nanotubes, phosphors, core-shell materials and metal oxides (Kruis et al. 1998; Rosner 2005). The flame synthesis methods are a straightforward and inherently scalable method. In addition, materials that are formed in a gas-phase flame at elevated temperature exhibit high purity (Helble 1998).

There are two common diffusion flame configurations: the normal diffusion flame (DF) configuration and the inverse diffusion flame (IDF) configuration. In the DF configuration, a gaseous fuel is injected into a surrounding flow of oxidizer (air or oxygen-enriched air). Many metal oxides have been synthesized using this flame configuration. In the DF configuration, it is difficult to control oxidation state of the metal oxides because of an abundance of oxygen. In contrast, an oxidizer is injected into a surrounding flow of fuel in the IDF configuration. In the inverse diffusion flame (IDF) configuration, nanoparticles of transition metal oxides can be synthesized with reduced oxidation state. The synthesis of reduced iron oxide nanoparticles in the IDF configuration has been recently reported (Kumfer et al. 2010). The IDF configuration can produce particles with significantly different morphology and crystallinity compared to those synthesized in the DF configuration (Kumfer et al. 2010; Pratsinis et al. 1996). To the best of our knowledge, the arsenic removal capacity of the IONPs synthesized in the gas-phase and their application to arsenic removal from water has not been investigated previously. Solution phase wet chemistry methods have been used in the past – they suffer from difficulty in scale up to commercially significant quantities suitable for widespread use.

Yu et al. (Yu et al. 2004) synthesized magnetite ( $\text{Fe}_3\text{O}_4$ ) nanocrystals using a solution of  $\text{FeO}(\text{OH})$ , oleic acid, and 1-octadecene by thermal decomposition of iron carboxylate salts, and Yavuz et al. (Yavuz et al. 2006) reported that the  $\text{Fe}_3\text{O}_4$  nanocrystals with the smallest particle size (12 nm) showed the highest arsenic removal capacity. Since gas-phase flame synthesis methods can produce IONPs with different oxidation states, with very small particle sizes, and with different morphologies, they offer the potential for cost effective arsenic removal from water.

The objectives of this study were 1) to characterize iron oxide nanoparticles (IONPs) with tunable oxidation state, synthesized in both the DF and IDF configurations under controlled flame conditions, and to investigate their arsenate ( $\text{As}(\text{V})$ ) removal efficacy, 2) to examine

their applicability in water treatment systems by comparing As(V) removal capacities of the IONPs with those for other iron oxide based adsorbents available commercially (e.g., Bayoxide E33<sup>®</sup> (E33)) or described in the literature (Chandra et al. 2010; Mayo et al. 2007), and 3) to study the effect of iron oxidation state and other particle characteristics on the As(V) removal capacities of IONPs.

## Materials and Methods

### Materials

For the synthesis of the IONPs in gas-phase flames, iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ , AlfaAesar, 99.5%) was chosen as the iron precursor. All compressed gases ( $\text{Ar}$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ ) were supplied from Praxair Inc. (San Ramon, CA) with stated purity of 99.5% or higher. In As(V) adsorption isotherm tests, As(V) stock solutions were prepared from reagent grade  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (AlfaAesar) in deionized water (MilliQ, Millipore Corp., Billerica, MA). The ionic strength of the testing solution was adjusted using sodium nitrate ( $\text{NaNO}_3$ , Sigma Aldrich). HEPES sodium salt (Fisher Scientific) used as a buffer at pH 7 (Kanematsu et al. 2011). All these chemicals were analytical grade and used as received without further purification.

### Gas-phase flame synthesis of IONPs

The IONPs were synthesized using either a DF or an IDF configuration, previously described in detail by Guo and Kennedy (Guo and Kennedy 2007) and Kumfer et al. (Kumfer et al. 2010) respectively. Schematics of both the DF and IDF configurations are shown in Figure 1A and 1B, respectively. Six different flames were studied, varying in their configuration and fuel/oxidizer conditions (Table 1). In the DF configuration, the fuel is injected through the central flow line surrounded by an oxidizer flow with or without dilution (Figure 1A) where maghemite,  $\gamma\text{-Fe}_2\text{O}_3$ , can be synthesized. In contrast, in the IDF configuration, the oxidizer (100%  $\text{O}_2$  or  $\text{O}_2$  diluted with  $\text{Ar}$ ) was injected through a central annulus of a coannular burner and an outer sheath flow of nitrogen was used to prevent oxygen contamination from room air (Figure 1B). The IDF configuration with different flame conditions (Flame A–E) was used to tune the oxidation state of particles by adjusting flame temperature, oxygen enrichment, fuel dilution, and fuel composition. The flame height was maintained at 30 mm. Iron pentacarbonyl was used as an iron precursor, and  $\text{H}_2$  (DF setup) or argon (IDF setup) was bubbled through the liquid precursor at constant temperature; the precursor was maintained in an ice bath at 0° C. The flame synthesized IONPs were collected in a system consisting of a funnel mounted coaxially to the flame, a filter housing assembly, and a vacuum system. The filter assembly housed three 47 mm Teflon filters (J020A047A, Advantec MFS Inc, Dublin CA). The overall particle collection yield ranged from 10 to 100 mg/hr, depending on flame conditions.

### Particle Characterization

The synthesized IONPs were suspended in MilliQ water and deposited on a 400 mesh copper TEM grid with a carbon/Formvar film (Ted Pella Inc. Redding CA. Prod # 01754-F); excess liquid was wicked away. The morphology of the IONPs was analyzed by transmission electron microscopy (TEM, Phillips, CM-12). TEM images were taken at an accelerating voltage of 120 kV. The particle crystalline phase was identified using a Scintag powder x-ray diffractometer (XRD) with  $\text{Cu K}\alpha$  radiation operated at 45 kV and 40 mA. The powder was scanned for  $2\theta = 10^\circ - 80^\circ$  with step size of  $0.02^\circ$  and step scan rate of  $2.4^\circ/\text{min}$ . The average domain size,  $D_{XRD}$  was calculated using Scherrer's formula (B. D. Cullity 2001),

$$D_{XRD} = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where the shape factor  $K$  is 0.9,  $\lambda$  is the incident x-ray wavelength ( $=1.54 \text{ \AA}$ ),  $\beta$  is the peak full width-half maximum (FWHM) at Bragg angle  $\theta = 35.6^\circ$ . The BET surface area of the IONPs was obtained using the  $N_2$  adsorption approach (AUTOSORB-1, Quantachrome Instruments, Boynton Beach, FL). Dynamic light scattering was used to determine the particle hydrodynamic size distribution and state of agglomeration/dispersion of the IONPs in water (BIC 90Plus, Brookhaven Instruments, Holtsville, NY). The effective diameter and number-weighted particle size distributions were calculated by the 90Plus software (Brookhaven Instruments). The effective diameter corresponds to the first cumulant of the correlation curve and for multimodal distributions it is weighted roughly by scattering intensity. The number-weighted particle size distribution is approximated by the correlation curve. The particle concentration for the DLS experiment was 50 mg/L in MilliQ (18.2 M $\Omega$ -cm) water and the solution was bath sonicated for one minute to disperse the particles. Zeta potential was measured by light scattering (ZetaPlus, Brookhaven Instruments Corp., NY). Particles were suspended in 1 mM KCl with particle concentration of 50 mg/L and the suspension was bath sonicated for five minutes before each sample measurement.

### Adsorption isotherms

As(V) adsorption isotherm tests were performed in completely mixed batch reactors (15 mL plastic centrifuge vials) at a solid concentration of 1.0 g/L. Duplicates of 10 mL solutions with a fixed amount of solid (10.0 mg) and different initial As(V) concentrations were prepared in the vials. The experiments were conducted at pH 7.0 and ionic strength of 0.02 M. The solution pH was maintained using 1 mM of HEPES, and ionic strength was adjusted using  $NaNO_3$ . The synthesized IONPs were sonicated for one minute to disperse the particles in the testing solutions using a probe sonicator and then shaken at 300 rpm using a shaker table for 3 days. After shaking, the IONPs were separated by centrifugation. After the separation, supernatants in the samples were carefully collected and acidified with 60% nitric acid and stored at 4°C before analyses. The pH was measured with a glass electrode and a pH meter with three points calibration (Mettler Toledo, Columbus, OH). As(V) concentrations were analyzed using inductively coupled plasma-mass spectrometry (7500i, Agilent Technologies, Wilmington, DE).

## Results and Discussion

### Particle characterization

The transmission electron microscopy (TEM) images of the six different IONPs as well as a commonly used nanostructured iron oxide adsorbent, Bayoxide E33 (E33), are shown in Figure 2. Particles formed by the DF configuration (i.e.,  $\gamma\text{-Fe}_2\text{O}_3$ ) are large compared to the particles formed in the IDF configuration mainly due to higher precursor loading in the DF configuration. For all samples, the images show large aggregates of primary particles. For the IDF configuration, the primary particle size, as determined by XRD, was smallest for sample A and largest for sample D. In contrast to flame-synthesized particles, where the particles are roughly spherical, the commercial sorbent (E33) primary particles are needle-like allowing for large surface area. The BET data for specific surface area for the flame-synthesized samples are shown in Table 2. The IONP synthesized in Flame A has the highest specific surface area of 207 m<sup>2</sup>/g, while  $\gamma\text{-Fe}_2\text{O}_3$  synthesized in the DF configuration has the lowest of 36 m<sup>2</sup>/g. The specific surface area for E33 (158.1 m<sup>2</sup>/g) (Kanematsu et al. 2011) is comparable to IONP produced in Flame D. The surface area

weighted diameters  $D_{SA}$  (Table 2) are comparable to the primary particle size seen in the TEM images and crystalline size measured by XRD.

The IDF offers a quite different temperature history of particles compared to the DF system. In the latter system, precursors are present in the fuel stream and particles begin to form inside the flame near the reaction zone. They are then convected through the flame. The high temperature promotes sintering at the relatively low melting point of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. On the other hand, the IDF drives freshly nucleated particles away from the flame into cold gases by thermophoresis and the particles have no opportunity to sinter and grow. The IDF configuration is ideal for the production of very small, high surface area, aerosols as Zhu and Pratsinis (1997) found in study of SiO<sub>2</sub> and SnO<sub>2</sub> synthesis in DF and IDF configurations.

Add this reference: Synthesis of SiO<sub>2</sub> and SnO<sub>2</sub> particles in diffusion flame reactors, Wenhua Zhu and Sotiris E. Pratsinis, *AIChE J.* 43, pp 2657 – 2664 (1997).

Powder XRD spectra for several samples are shown in Figure 3. The spectra show peaks for spinel ferrites. Because this spinel structure is characteristic of both maghemite and magnetite, it is hard to distinguish between these ferrites. The crystalline diameter,  $D_{XRD}$ , is determined by eq. 1 and these data are also shown in Table 2. In general, the particle size increases with increasing flame temperature.

The distribution of hydrodynamic diameters as measured by DLS is shown in Figure S1 (the supporting information). The mean particle size in solution for all samples is larger than the primary particle size seen in the TEM images, confirming that the particles form aggregates in solution. For samples produced in Flames A–E, the size distributions are broad – and Flames B and D produced IONPs with a bimodal distribution. Although TEM images of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> show a distinct bimodal distribution as observed previously by Guo and Kennedy (Guo and Kennedy 2007), DLS data do not reflect this bimodality. Since scattering intensity is proportional to  $d^6$ , the scattering signal from large particles will dominate signals from smaller particles and this likely explains the apparent absence of the small particle mode from the DLS data. The mean number-weighted diameter and intensity-weighted diameter data are also shown in Table 2.

To quantify the oxidation states of iron in the IONPs synthesized in Flames A–E, Kumfer et al. (Kumfer et al. 2010) used XANES spectroscopy to analyze IONPs produced under identical conditions; they compared sample spectra to standard reference materials such as Fe(0) foil, magnetite, and Fe(III) oxides. The results from their XANES data are summarized in Table 2. Both  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> synthesized in the DF configuration and the IONP synthesized in Flame A have only Fe(III) valence. The IONPs synthesized in Flames B, C, and D have increasing Fe(II) content, and the IONP synthesized in Flame E includes zero valent iron (ZVI) along with Fe(II) and Fe(III). Further evidence of mixed oxidation states in the IONPs synthesized in Flames B – D is provided by magnetic data obtained using a vibrating sample magnetometer (VSM)(Kumfer et al. 2010). The slight coercive force measured for all particles (Table 2) can be attributed to a non-monodispersed particle distribution; a few large particles in the distribution contribute to the coercivity

The values of the zeta potential of the IONPs at pH 7 are listed in Table 2. The zeta potential, an approximation to the surface potentials of particles in solution, was high (> 30 mV) for the IONPs synthesized in Flames A, D and E, suggesting electrostatic stabilization of the particles in solution. In contrast, the IONPs synthesized in Flames B, C and the DF configurations showed lower zeta potentials, indicating lower particle stability.

## As(V) removal capacity

As(V) adsorption isotherms were obtained at pH 7 for the six different IONPs and compared with a commonly used goethite-based adsorbent (E33) (Kanematsu et al. 2010) and Fe<sub>3</sub>O<sub>4</sub> nanocrystals synthesized by thermal decomposition of iron carboxylate salts (Yavuz et al. 2006) in Figure 4A. On a mass basis (Figure 4A), As(V) adsorption capacities of the six IONPs are rated as follows: Flame A > Flame B > Flame E > Flame C > Flame D >  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> synthesized in the DF configuration. Hence, it is found that the IDF-IONPs have much higher As(V) adsorption capacities than that of the DF-IONP. Almost all IDF-IONPs showed higher adsorption capacity than that of E33 on a mass basis. The adsorption capacity of the fully oxidized IDF-IONPs synthesized in Flame A, maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), is three to four times higher than that of E33 on a mass basis. Therefore, the IDF-IONPs synthesized in Flame A could be used for As(V) removal in water based on their As(V) adsorption capacity. In contrast,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> synthesized in the DF configuration showed much lower adsorption capacity than E33, although its chemical composition is identical to the IDF-IONPs synthesized in Flame A. This is probably due to much larger particle size of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> synthesized in the DF configuration.

The specific surface area normalized adsorption isotherms are shown in Figure 4B. The specific surface area normalized adsorption capacity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> synthesized in the DF configuration is quite similar to that of the IDF-IONPs synthesized in Flame A (Figure 4B). Therefore, the difference in the adsorption capacity between these two materials is due to different particle sizes rather than differences in the number of active surface sites per area. It may be possible, therefore, that the DF configuration could produce IONPs with high adsorption capacity if their particle sizes were reduced to below approximately 10 nm by controlling the flame characteristics.

Yavuz et al. (Yavuz et al. 2006) synthesized monodisperse Fe<sub>3</sub>O<sub>4</sub> nanocrystals with different particle sizes (12, 20, and 300 nm) and demonstrated their As(V) and As(III) removal capacities at pH 8. In their studies, the Fe<sub>3</sub>O<sub>4</sub> nanocrystals were synthesized using a mixture of FeO(OH), oleic acid, and 1-octadecene by thermal decomposition of iron carboxylate salts as described in Yu et al. (Yu et al. 2004). The size of the Fe<sub>3</sub>O<sub>4</sub> nanocrystals strongly affected arsenic removal capacities, and the Fe<sub>3</sub>O<sub>4</sub> nanocrystals with 12 nm diameter showed the highest adsorption capacity, which is equivalent to approximately two hundred times higher arsenic removal capacity than commercially available Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Yean et al. 2005). As(V) adsorption isotherms of the six different IONPs at pH 7 are compared with that of Yavuz et al. 12 nm Fe<sub>3</sub>O<sub>4</sub> nanocrystals at pH 8 in Figure 4A. Although As(V) adsorption on iron oxide decreases with increasing pH (Dixit and Hering 2003; Gimenez et al. 2007), the IDF-IONPs generally offer superior As(V) removal compared with the magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanocrystals synthesized by Yavuz et al. (Yavuz et al. 2006), especially at very low arsenic concentrations.

## Effect of oxidation state on As(V) removal capacity of IONPs

The oxidation states of iron in the IDF-IONPs were determined previously by our laboratory using XANES (Kumfer et al. 2010). The effect of oxidation state of the IDF-IONPs on their As(V) surface area normalized removal capacities at three different As(V) concentrations (10, 100, and 1,000  $\mu$ g/L as As) is shown in Figure 5. The Fe(II)/Fe(III) ratio is used as an indication of the oxidation state of iron in the IONPs. It can be seen that As(V) adsorption capacity increased with a decrease in Fe(II)/Fe(III) for the IDF-IONPs. Since Su and Puls (Su and Puls 2008) reported that no chemical reduction of As(V) could be observed in magnetite suspensions, chemical reduction of As(V) to As(III) is probably not the reason for the lower As(V) adsorption on more reduced IONPs. Although the data in Figure 5 are suggestive of an effect of iron oxidation state on adsorption capacity, unambiguous

conclusions about this effect cannot be derived from our data because there is a strong cross-correlation between the oxidation state and the specific surface area of the particles in moving from material A to material D. Even though the data in Figure 4B have been normalized by specific surface area this may not completely remove the effect of surface area because arsenate accessible surface area in solution may differ from nitrogen accessible surface area under vacuum. Differences in zeta potential reflect differences in surface potentials but may also be related to particle aggregation during the batch experiments. Further, the IONPs synthesized in Flame E, which contains 14% of Fe(0) and 12% of Fe(II), did not follow the trend in Figure 5, instead exhibiting a slightly higher adsorption capacity than the more oxidized IDF-IONPs synthesized in Flames C and D (Figures 4A and 4B). Kanel et al. (Kanel et al. 2005) reported that ZVI is susceptible to oxidation in water and gradually oxidized to magnetite and/or maghemite corrosion products mixed with lepidocrocite ( $\gamma$ -FeO(OH)) over 60 days. The magnetite/maghemite products derived from oxidized ZVI might contribute to the increase in As(V) adsorption capacity for the IONPs synthesized in Flame E. Moreover, the IONPs synthesized in Flame E also showed higher zeta potential at pH 7.0 than the IONPs synthesized in Flames C and D. The reason for the higher zeta potential of this IONP is not clear.

## Conclusion

This study demonstrates that IONPs synthesized in flames are promising adsorbents for the removal of As(V) from water with the additional attractive property of magnetization that can be used for separation and manipulation. An increase in the Fe(III)/Fe(II) ratio resulted in a higher arsenic adsorption capacity, with fully oxidized iron oxide (Flame A) particles showing an approximately four-fold increase in adsorption capacity compared to a commercial sorbent (Bayoxide E33). Although inverse diffusion flames are capable of producing low oxidation state particles, their major benefit in the case of As adsorption is their ability to yield very small, unsintered particles that lead to high surface area materials. A normal diffusion flame (DF) can also produce maghemite but with significantly lower specific surface area. Since flame synthesis has significant potential for economical large-scale production of IONPs, adoption of an IDF synthesis route may lead to reduction in the currently high cost of adsorption systems for arsenic removal from water (Colby et al. 2010).

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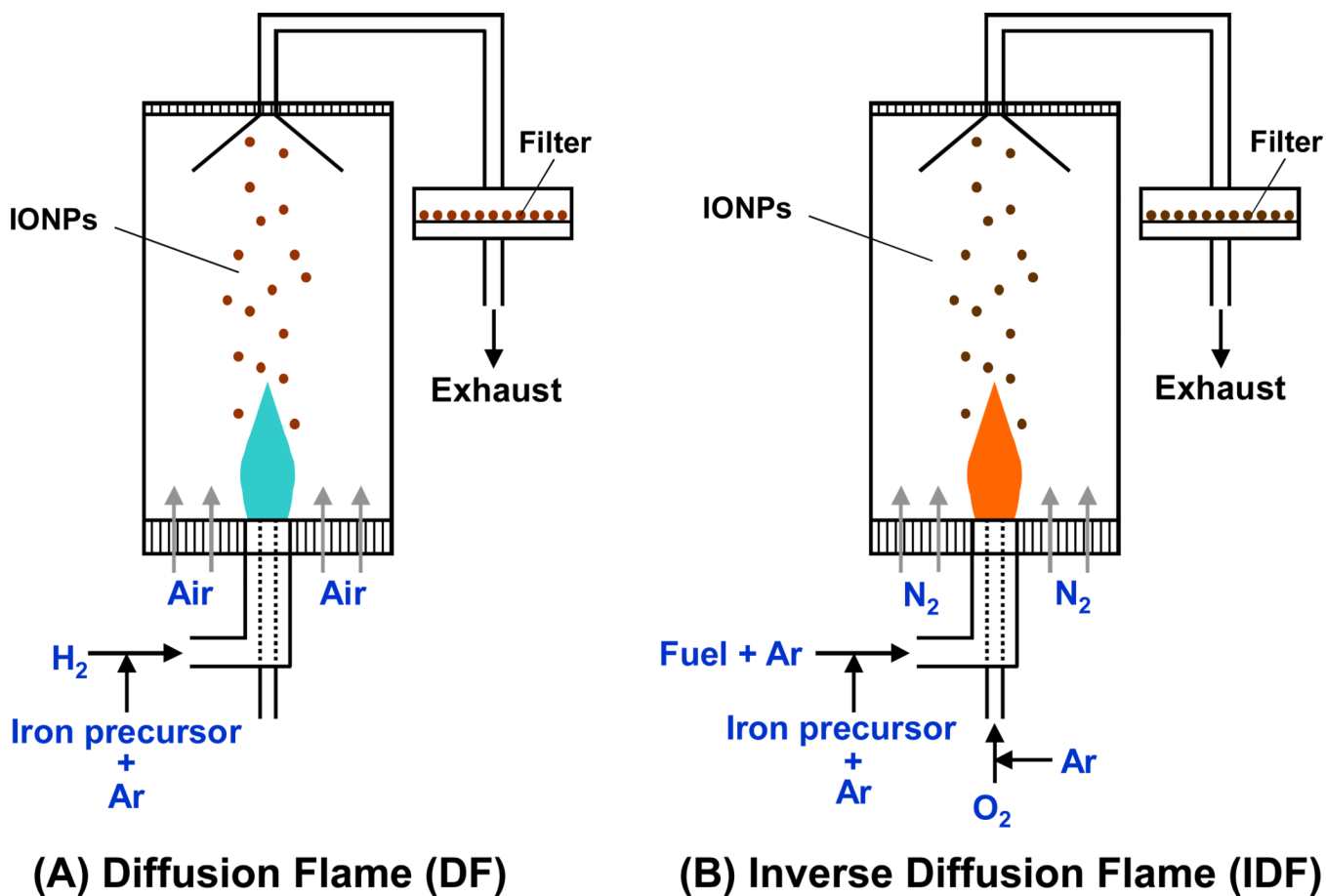
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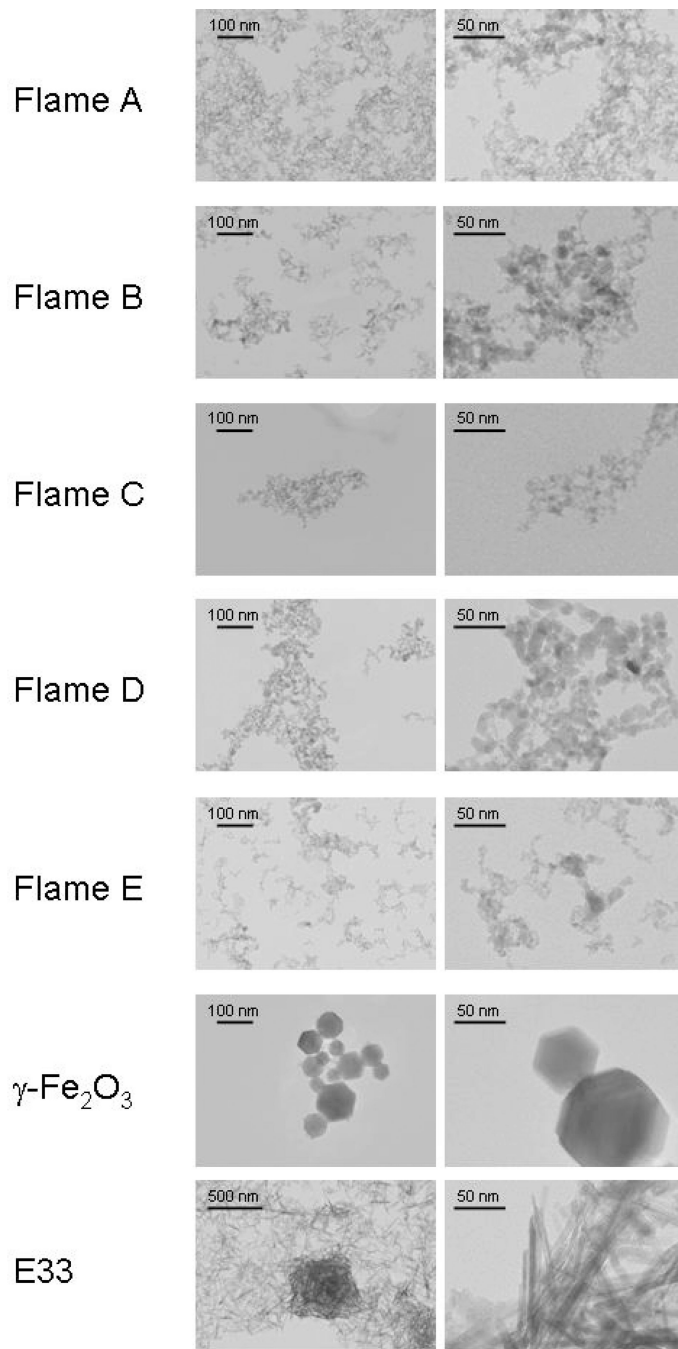
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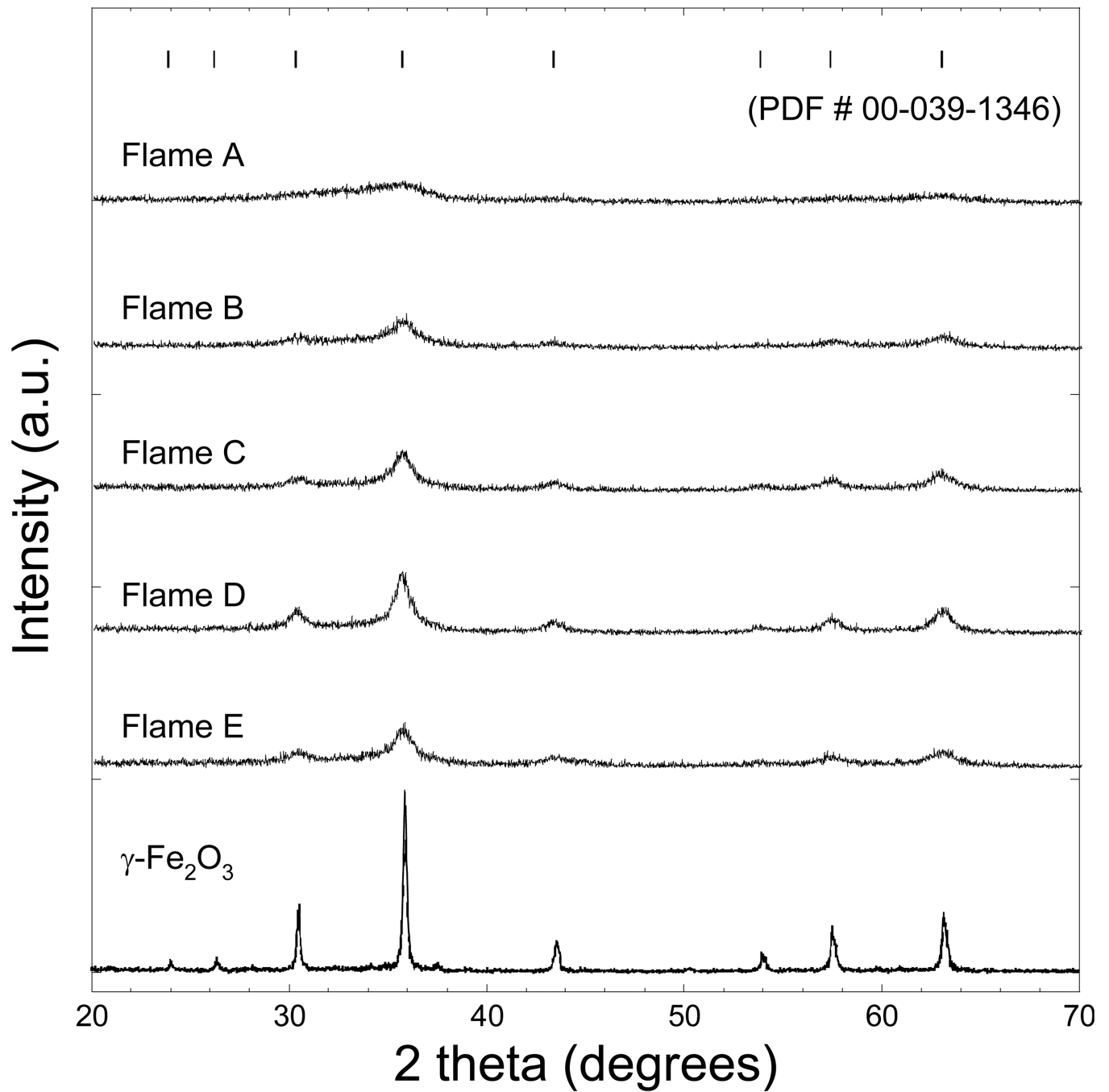
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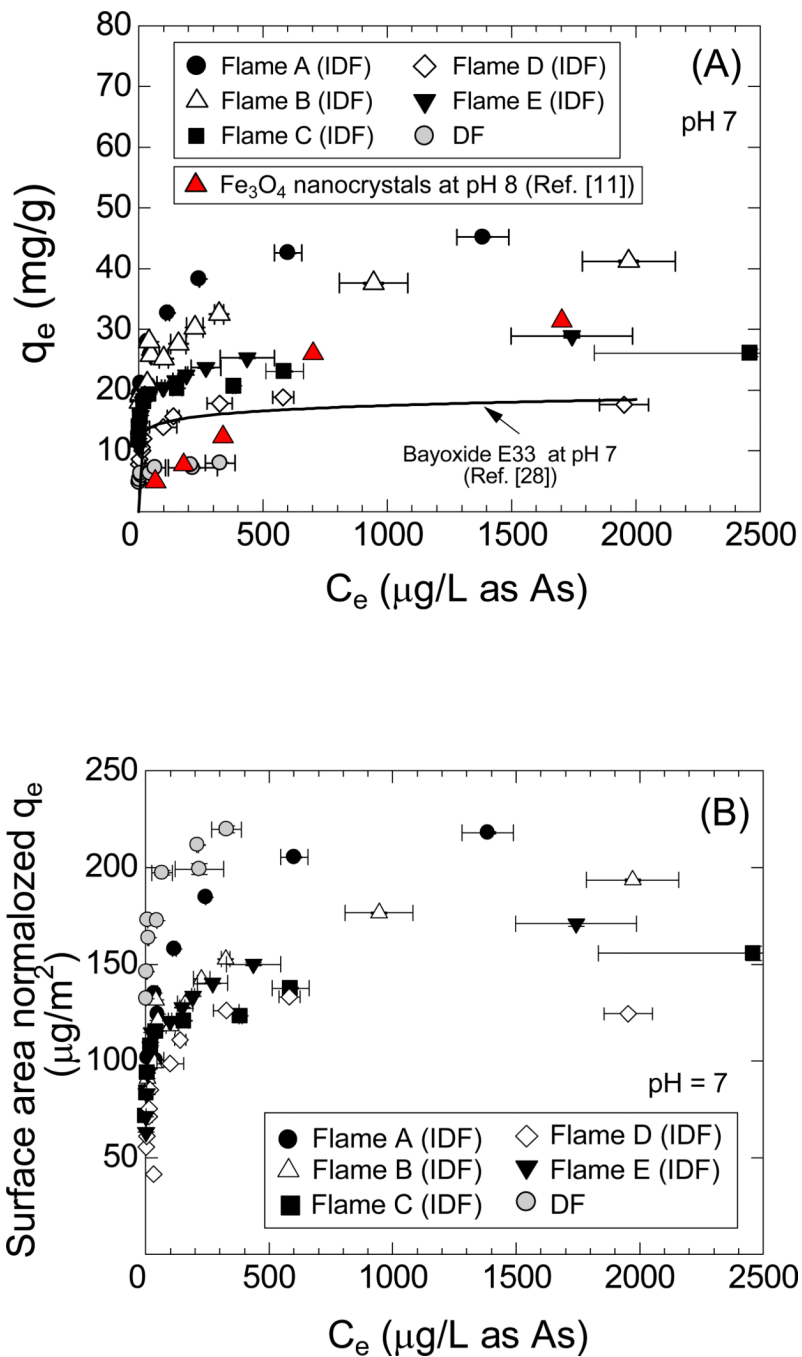
**Figure 1.** Schematic of the flame configurations to synthesize iron oxide nanoparticles (IONPs). In the diffusion flame (DF) configuration (A), the fuel is injected into the center annulus with air on the outside. In the inverse diffusion flame (IDF) configuration (B), the oxidizer is injected into the center annulus with fuel injected in the outside concentric flow.



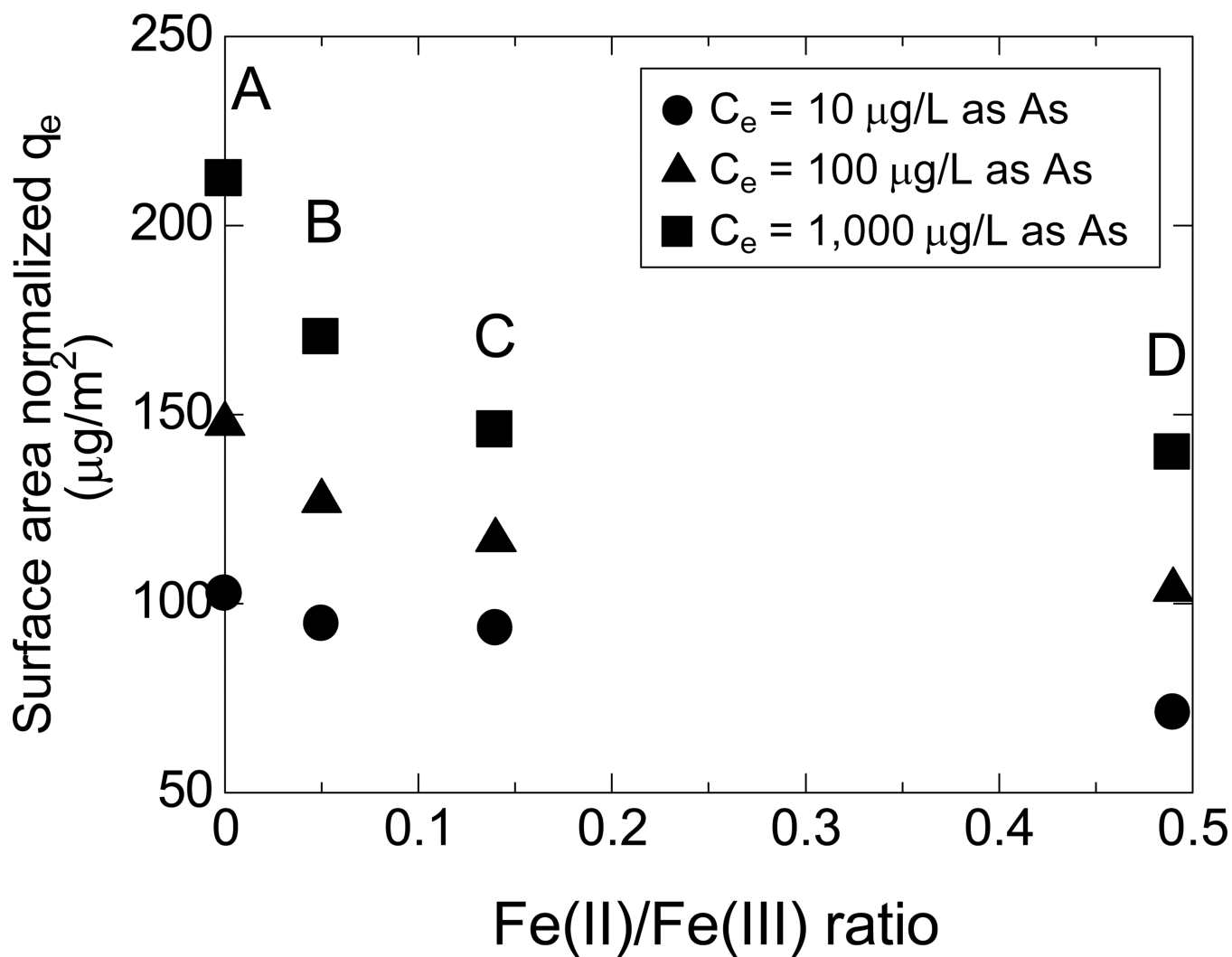
**Figure 2.** Transmission electron microscope (TEM) images of the flame-synthesized IONPs (Flames A–E correspond to the IONPs synthesized in the IDF configuration, and maghemite,  $\gamma\text{-Fe}_2\text{O}_3$  corresponds to the IONPs synthesized in the DF configuration) and a goethite-based commercial sorbent (E33). For all samples, the particles form large aggregates composed of smaller primary particles.



**Figure 3.** Powder X-ray diffraction patterns of flame synthesized iron oxide samples. Vertical ticks represent main diffraction peaks for maghemite.



**Figure 4.** (A) As(V) adsorption isotherms of the flame-synthesized IONPs at pH 7. As(V) adsorption isotherms of  $\text{Fe}_3\text{O}_4$  nanocrystals (Yavuz et al. 2006) and a goethite-based common adsorbent, E33(Kanematsu et al. 2011) are included for reference. (B) Surface area normalized As(V) adsorption isotherms of the flame synthesized IONPs at pH 7.



**Figure 5.** Influence of oxidation state, indicated by Fe(II)/Fe(III) ratio, on the surface area normalized As(V) adsorption capacity of the IONPs (Flames A to D) at three different liquid phase equilibrium As(V) concentrations.

Table 1

Flow conditions used to synthesize iron oxide nanoparticles.

Sample Name	Flame configuration <sup>1</sup>	Fuel	Oxidizer	Fuel line flow rate (L/min)			Oxidizer line flow rate (L/min)			$T_{ad}$ (K) <sup>2</sup>
				Fuel	Ar	Ar <sub>precursor</sub>	O <sub>2</sub>	Ar		
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	DF	H <sub>2</sub>	Air	0.1	-	-	0.1	-	2200	
Flame A	IDF	CH <sub>4</sub>	O <sub>2</sub>	0.204	0.983	0.013	0.14	0.56	2150	
Flame B	IDF	CH <sub>4</sub>	O <sub>2</sub>	0.084	1.103	0.013	0.128	0.043	2150	
Flame C	IDF	CH <sub>4</sub>	O <sub>2</sub>	0.12	1.067	0.013	0.19	-	2450	
Flame D	IDF	CH <sub>4</sub>	O <sub>2</sub>	0.18	1.007	0.013	0.25	-	2650	
Flame E	IDF	C <sub>2</sub> H <sub>4</sub>	O <sub>2</sub>	0.072	1.115	0.013	0.129	0.021	2450	

<sup>1</sup>DF, diffusion flame; IDF, inverse diffusion flame.

<sup>2</sup>data from Kumfer *et al.* Kumfer et al. 2010) except, for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, data from Guo and Kennedy (2007).

Table 2

Summary of particle properties.

Sample Name	BET Surface Area (m <sup>2</sup> /g)	D <sub>SA</sub> (nm)	D <sub>XRD</sub> (nm)	D <sub>NWM</sub> (nm) <sup>1</sup>	D <sub>IWM</sub> (nm) <sup>2</sup>	M <sub>S</sub> (emu/g) <sup>3</sup>	H <sub>c</sub> (Oe) <sup>3</sup>	ζ (mV)	Percent of total iron in iron oxides <sup>3</sup>		
									Fe(0)	Fe(II)	Fe(III)
γ-Fe <sub>2</sub> O <sub>3</sub>	36	29	36	325.7	387.8	n/a	n/a	2.4	-	-	100
Flame A	207	4.9	2.9 <sup>3</sup>	63.6	144.2	6.5	13	35.0	-	-	100
Flame B	213	4.8	7.9 <sup>3</sup>	88.2	195.0	24	19	12.9	-	~5	~95
Flame C	168	6.4	11 <sup>3</sup>	124.7	293.8	42	30	7.4	-	12	88
Flame D	141	8.2	12 <sup>3</sup>	83.5	209.4	57	60	34.6	-	33	67
Flame E	169	6.0	n/a	74.7	150.6	60	76	30.5	14	10	76

<sup>1</sup> Number weighted mean diameter.

<sup>2</sup> Intensity weighted mean diameter.

<sup>3</sup> data from Kumfer et al. (Kumfer et al. 2010)