

# Analytical Methods

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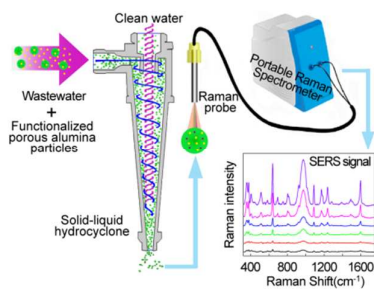
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A novel method for reliable on-site characterization of aromatic compounds adsorbed on porous particle with surface enhanced Raman spectroscopy (SERS)

## ARTICLE

# Reliable on-site characterization of aromatic compounds adsorbed on porous particle with SERS in a dynamic adsorption-hydrocyclone separation process

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A novel method for reliable on-site characterization of aromatic compounds adsorbed on porous particle with surface enhanced Raman spectroscopy (SERS) in a dynamic adsorption-hydrocyclone separation process (DAHS) was introduced. Aromatic compounds found in printing and dyeing wastewater were adsorbed on functionalized porous alumina particles (FPAPs). The SERS-active FPAPs were prepared by decorating and growing silver nanoparticles (Ag NPs, ~70 nm diameter) on the surface of porous alumina particles (PAPs). Samples were then characterized with a portable Raman spectrometer. SERS offers quantitative analyses of the pollutants adsorbed on the surface of FPAPs directly and the quantity of benzidine adsorbed on porous particles was 20.5mg/kg. It shows that the SERS-DAHS technique could be readily applied to the quantitative characterization of aromatic compounds adsorbed on SERS-active FPAPs. Furthermore, both qualitative and quantitative detection of aromatic compounds in wastewater produced on-site were readily accomplished using the SERS-DAHS method and its analytical ability compares well with GC-MS and the detection results deviating between these two techniques was less than 10%. The results demonstrate that the SERS-DAHS method is straightforward, rapid, and preferable for the real-time detection and quantitative characterization of aromatic compounds/pollutants adsorbed on porous materials.

## Introduction

Aromatic compounds are well-known for their toxic, carcinogenic and mutagenic effects.<sup>1</sup> They are widely used as ingredients and solvents in various printing and dyeing applications,<sup>2</sup> leading to the production of about  $11.3 \times 10^8$  tons of wastewater each year in China alone. These compounds pose a serious threat to aquatic life as well as human health if they are not adequately remediated before environmental release.<sup>3</sup> Therefore, it is very important to develop effective wastewater monitoring and treatment methods to be employed on-site at industrial facilities. Various technologies are used for printing and dyeing wastewater treatment, including membrane filtration, reverse osmosis, precipitation, ion exchange, and electrochemical techniques.<sup>4-8</sup> These processes each have disadvantages and limitations, such as high cost, poor removal efficiency, or generation of secondary pollutants. Recently, adsorption using porous adsorbents has been shown to be an efficient and effective method for removing pollutants from wastewater.<sup>9</sup> Many studies have explored the different adsorption selectivity of porous materials in the laboratory,<sup>10-12</sup>

but measurement of the properties of pollutants adsorbed on the surfaces of these materials, especially quantitative detection from on-site waste streams, has yet to be addressed.

Surface-enhanced Raman spectroscopy (SERS) is an ultrasensitive, ultra-rapid, and widely-applicable analysis technique, which can be used as both a quantitative and a qualitative detection tool.<sup>13-15</sup> SERS offers extremely low detection limits, on the order of single molecules on the surfaces of extremely small samples. This is due to the enhancement of the electromagnetic field induced by the resonance of plasmon on nanostructured metallic surfaces.<sup>16</sup> The ability of SERS to efficiently measure small quantities of material has led to its being widely employed in the detection of hazardous material and the analysis of chemical and biological samples.<sup>17-20</sup> Furthermore, This technique has also been successfully used for on-site detection of pollutants by preparing specific SERS-active substrates.<sup>21</sup>

Due to the large throughputs associated with wastewater treatment processes, it is equally important to be able to separate adsorbents from wastewater efficiently as it is to be able to detect pollutants. The centrifugal separation devices

known as solid-liquid hydrocyclone have been successfully used to isolate porous particles with adsorbed aromatic compounds so that these contaminants could be characterized. Solid-liquid hydrocyclone are widely used in the petrochemical and papermaking industries, as well as in the treatment of environmental contaminants,<sup>22-24</sup> as they offer conveniently small sizes (see Table S1 in ESI†) and have no moving parts. Extensive research on the ability of solid-liquid hydrocyclone to separate solids of different structures and sizes have proven that these devices are capable of satisfying the separation requirements of a wide variety of applications, with a separation efficiency of more than 85% when used with solid particles of diameters larger than 3  $\mu\text{m}$ .<sup>25-26</sup>

In this study, we focus on combining SERS with solid-liquid hydrocyclone as a potential strategy for reliable on-site characterization of aromatic compounds adsorbed on porous alumina particles. First, the SERS-active FPAPs were prepared by decorating and growing silver nanoparticles (Ag NPs) on the surface of porous alumina particles (PAPs) and their characterization was also evaluated (see Table S2 in ESI†). FPAPs were mixed with wastewater and separated using a solid-liquid hydrocyclone after adsorption was complete. SERS analysis was used to quantify the amount of pollutants adsorbed on the surface of FPAPs. In addition, a method combining SERS with dynamic adsorption-hydrocyclone separation (heretofore referred to as the SERS-DAHS process) was used on-site to investigate the aromatic compounds in printing and dyeing wastewater. The results demonstrate that the SERS-DAHS technique could be readily employed on-site to quantitatively characterize aromatic compounds found in industrial wastewater.

## Experimental

### Materials

Silver nitrate (99%), stannous chloride (>99%), ascorbic acid, and hydrochloric acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Porous alumina particles (PAPs) were

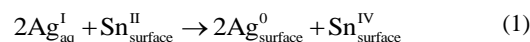
obtained from the Dalian Institute of Chemical Physics of the Chinese Academy of Sciences. All other reagents were analytical grade and were purchased from Aladdin-Reagent Co., Ltd. (Shanghai, China). All solutions were prepared with 18 M $\Omega$ -cm deionized water obtained with a Mili-Q System (Billerica, MA, USA).

### Apparatus

Scanning electron microscope (SEM) images of the prepared Ag NPs on the surface of porous alumina particles were acquired using a field-emission scanning electron microscope (NOVA NanoSEM450, FEI Inc., U.S.A). Raman spectra were recorded with a small portable Raman spectrometer (BWS415, B&W Tek Inc., U.S.A) using an excitation wavelength of 785 nm, a resolution of 5  $\text{cm}^{-1}$  and a beam diameter of 10  $\mu\text{m}$ .

### Preparation of functional porous material

Silver seeds with a narrow size distribution were decorated on the surface of PAPs by electroless deposition as follows: First, PAPs were immersed in a mixture aqueous including  $\text{SnCl}_2$  (0.02M) and  $\text{HCl}$  (0.01M) for 2 min in order to make sure  $\text{Sn}^{2+}$  deposit on the surface of PAPs. The PAPs were washed thoroughly with deionized water and acetone for several times and then dried at 70  $^\circ\text{C}$ . Second, The PAPs were dipped into an aqueous solution of  $\text{AgNO}_3$  (0.005M) for 2 min to generate Ag seeds on the surface of PAPs, followed by the same drying process used in the first step. These two steps constituted one deposition cycle and were repeated six times to provide a high density of silver seeds as shown in equation (1).<sup>27</sup>



Third, in situ growth of silver seeds was utilize to complete the controlled assembly of properly-sized Ag NPs on the surface of PAPs: PAPs with surface deposited silver seeds were immersed in a mixture solution consisted of 5ml ascorbic acid (100mM) and 10ml silver nitrate (10mM) for several minutes,<sup>28</sup> then FPAPs were completely synthesized.

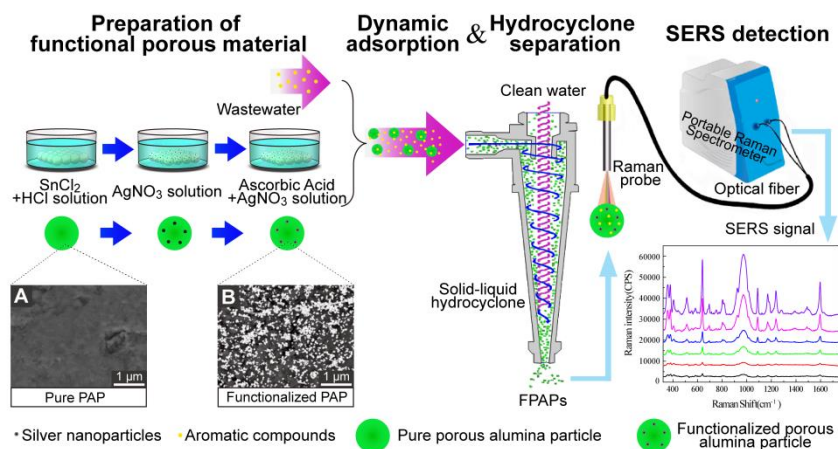


Fig. 1 Schematic illustration of SERS-DAHS for Reliable quantitative SERS analysis of aromatic compounds in a dynamic adsorption-hydrocyclone separation process

## Detection method

The SERS-DAHS method (shown in Figure 1) was designed for reliable on-site characterization of aromatic compounds in a dynamic adsorption-hydrocyclone separation process. First, Ag NPs were decorated on the surface of PAPs to produce FPAPs. FPAPs were mixed with wastewater to initiate adsorption, and then the mixture was pumped into solid-liquid hydrocyclone. FPAPs and adsorbed pollutants were separated from the mixture using the centrifugal force field and isolated in the underflow of the solid-liquid hydrocyclone. Due to the presence of Ag NPs on the surface of FPAPs, SERS could be used to observe the uneven silver films with regions of high curvature and gaps between Ag NPs.<sup>29</sup> Confined electromagnetic fields, commonly referred to as “hot spots”, originate from localized surface plasmons excited in these areas.<sup>30</sup> As a result, SERS signals can be collected directly from the surfaces of FPAPs which were taken from the underflow of the hydrocyclone and dried under nitrogen at 30 °C. Meanwhile, Raman spectra of aromatic compounds in wastewater before and after DAHS were achieved using silver colloidal SERS substrates (see Text S2 in ESI†).

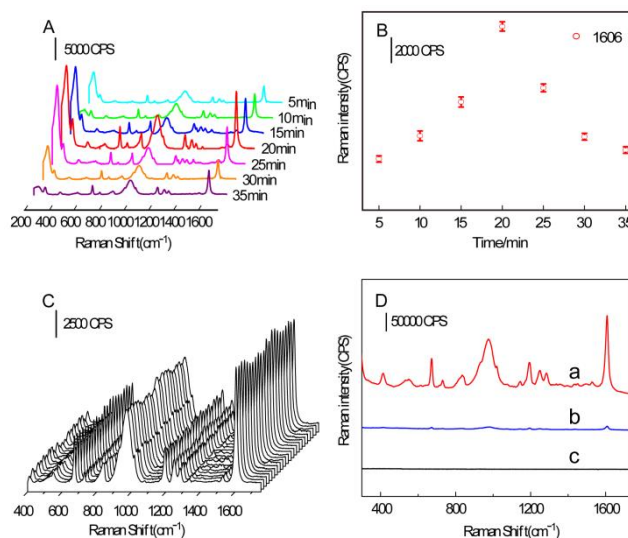
## Results and Discussion

### Characterization and evaluation of the SERS-activity of FPAPs

The qualities of SERS-active of FPAPs are closely related with the performance of SERS detection using these substrates. Ag NPs with appropriate diameters could provide strong SERS activity to FPAPs. The diameters of Ag NPs are affected by factors such as the concentration of the soak solution, soak time, and the surface energy of the porous particles.<sup>31</sup> Herein, the diameter of Ag NPs was controlled by changing the soak time of PAPs in a solution of ascorbic acid and silver nitrate. The SERS spectra of benzidine adsorbed on FPAPs prepared using various soak times (Figure 2A-B) reveals that satisfactory signal intensity can be obtained when the soak time is 20 minutes. SEM images of silver particles for various soak times was showed Figure S2 in ESI. Moreover, representative SEM images of pure PAPs (Figure 1A) and FPAPs (Figure 1B) show that Ag NPs have been evenly deposited on the surface of PAPs after this amount of time. Figure 1B shows that Ag NPs have a spherical shape within a narrow size distribution, with diameters of approximately 70 nm. Size distribution of Ag NPs soaked for 20min was showed Figure S3 in ESI. This can also be confirmed by the comparison of the SERS spectra of FPAPs and pure PAPs (shown in Figure 2D). To further evaluate SERS activity of FPAPs quantitatively, the SERS spectrum of *p*-aminothiophenol (*p*-ATP) solution dropped on the surface of FPAPs and normal Raman spectrum of bulk *p*-ATP were compared, the corresponding enhancement factor (EF) was calculated (see Text S1 in ESI†) to be about  $1.2 \times 10^5$ .

SERS is an important analytical method that can be used to obtain fingerprint information of a target molecule. The uniformity and reproducibility of the active substrate are crucial for using SERS in real-life applications. SERS spectra of

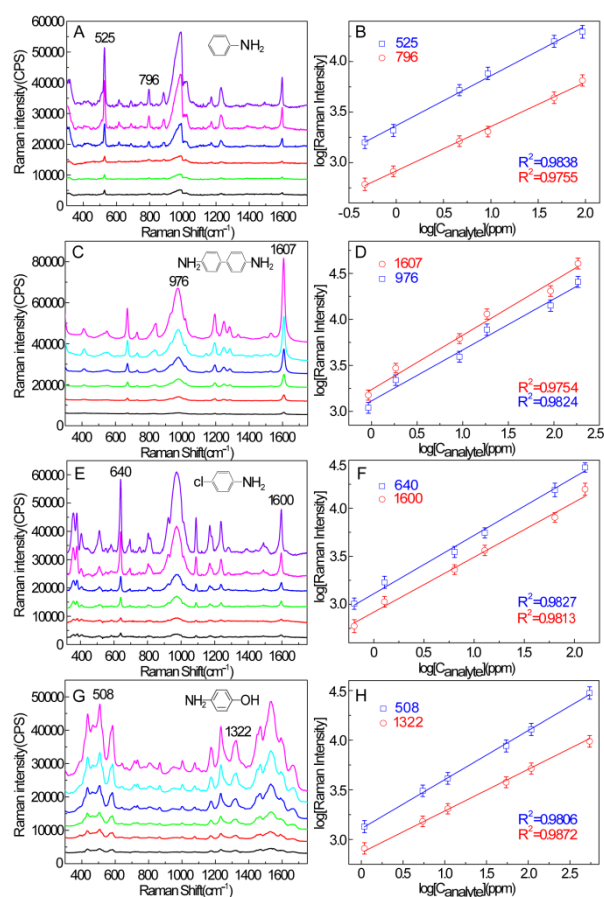
benzidine with a concentration of  $3 \times 10^{-4}$  M were recorded at twenty-two randomly-selected detection points on the surface of FPAPs using a laser power of 20 mW and an integration time of 20 s (Figure 2C). The consistency of these spectra demonstrates the uniformity and reproducibility of the active substrate. Taking the intensity change of the Raman bands at  $976 \text{ cm}^{-1}$  as an example, the relative standard deviation of the intensity across all twenty-two points is 5%, which indicates the uniformity of the substrate is fairly good.



**Figure 2** (A) SERS spectra of  $10^{-4}$  M benzidine using various soak times. (B) Raman intensity for different soaking times. Laser power: 20 mW; integration time: 20 s. (C) SERS spectra of benzidine with the concentration of  $3 \times 10^{-4}$  M at twenty-two random selected detection points on the surface of FPAPs. Soak time is 20 minutes; laser power: 20 mW; integration time: 20 s. (D) SERS spectra of benzidine ( $5 \times 10^{-4}$  M) adsorbed (a) on the surface of functionalized FPAPs and (b) on the surface of pure PAPs and (c) SERS spectra of FPAPs without any chemicals.

### Calibration curve library of Raman intensity against to concentration for varieties of aromatic compounds

A calibration curve library of Raman intensity versus concentration for various aromatic compounds (Figure 3) was built using SERS spectroscopy with silver colloidal substrates on solutions of four groups of aromatic compounds with known concentrations. It is notable that the log-log plots of Raman intensity at  $525 \text{ cm}^{-1}$  and  $796 \text{ cm}^{-1}$  versus a series of aniline concentrations ( $0.5$  to  $100 \text{ mgL}^{-1}$ ) show a clear linear relationship ( $R^2=0.9838$ ,  $R^2=0.9755$ ) as seen in Figure 3B. The same quantitative method was employed for solutions of benzidine, parachloroaniline and 4-aminophenol, as shown in Figure 3C-H. All four aromatic compounds show similar quantitative results. The good linear relationship of the log-log plot is in agreement with previous reports on SERS analysis of substituted aromatic compounds.<sup>21,33</sup> Using this calibration curve library, the exact concentration of aromatic compounds in wastewater before and after DAHS can be conveniently obtained by on-site SERS detection.



**Fig. 3** Calibration curve library of intensity against to concentration of various aromatic compounds. Laser power 20; mW; integration time: 20s. Error bars represent the mean value of three replicate samples and corresponding standard deviation.

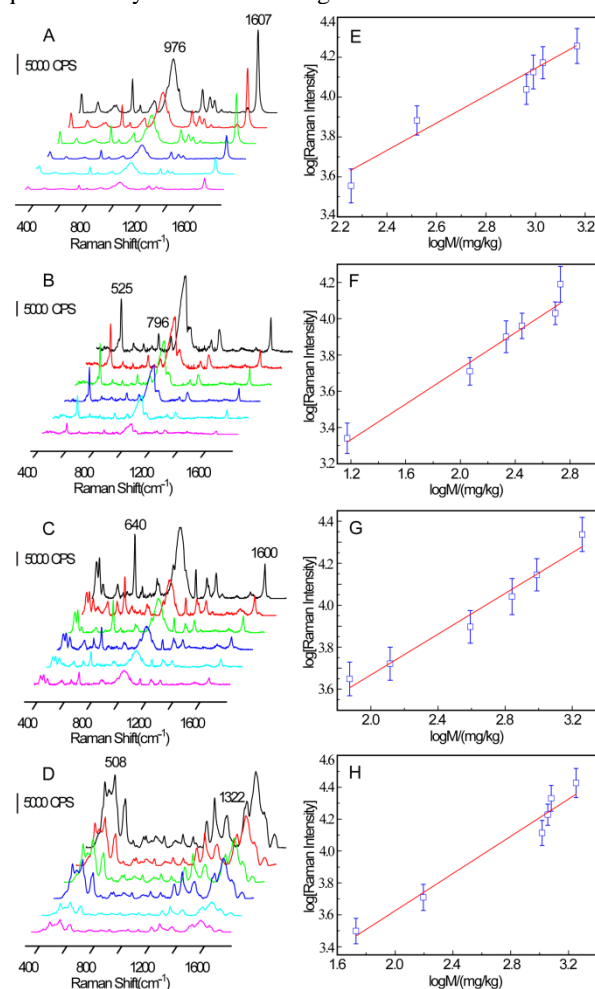
### Combination of solid-liquid hydrocyclone with SERS for on-site characterization of aromatic compounds

The usage of a solid-liquid hydrocyclone in combination with SERS for on-site quantitative detection of aromatic compounds was investigated using artificially-produced model samples of wastewater containing aromatic compound as samples of well-known priority pollutants. The pollutants in the wastewater were partly adsorbed on the surface of FPAPs, and then separated from wastewater with a solid-liquid hydrocyclone. FPAPs with adsorbed aromatic compounds were captured from the underflow of the solid-liquid hydrocyclone, dried under nitrogen at 30 °C and analyzed by SERS under the optimized conditions described above. SERS spectra for four kinds of aromatic compounds with six different unknown concentrations respectively on the surface of FPAPs are shown in parts Figure 4A-D. Meanwhile, SERS spectra of aromatic compounds in wastewater before and after DAHS were recorded using silver colloidal SERS substrates. By comparing the Raman intensity at 640  $\text{cm}^{-1}$  (for parachloroaniline) with SERS spectra from the calibration curve library established previously (Figure 3), the exact concentration of aromatic compounds in the wastewater before and after DAHS was obtained. The quantity of adsorbed

pollutants on 1 kg of FPAPs ( $M$ ) could be obtained by equation (2):

$$M = (C_i - C_o) \times Q_f / (Q_s \times E) \quad (2)$$

where  $Q_s$  is the feed quantity of FPAPs,  $Q_f$  is the wastewater flow rate,  $E$  is the separation efficiency of different feed concentrations (99%, see Figure S4 in ESI†),  $C_i$  and  $C_o$  are the concentrations of aromatic compounds in the wastewater before and after DAHS respectively. The SERS intensity of vibrational bands is quite sensitive to the concentration of aromatic compounds on the surface of FPAPs.<sup>33</sup> Log-log curves of intensity against the quantity of pollutants adsorbed on 1 kg of FPAPs are plotted in parts E-H of Figure 4. (detailed data see Table S3 in ESI†) The plots show a good linear relationship between the intensity of representative peaks and the quantity of adsorbed pollutant, demonstrating that the amount of pollutant adsorbed on the surface of FPAPs could be accurately and quantitatively determined using SERS detection.



**Figure 4** SERS spectra for (A) benzidine, (B) aniline, (C) parachloroaniline, (D) 4-aminophenol with six different concentrations respectively on the surface of FPAPs, and the log-log curves of intensity against to the quantity of adsorbed pollutants on 1 kg PAPs for (E) benzidine at 976  $\text{cm}^{-1}$ , (F) aniline at 525  $\text{cm}^{-1}$ , (G) parachloroaniline at 640  $\text{cm}^{-1}$ , (H) 4-aminophenol at 508  $\text{cm}^{-1}$ . Error bars represent the mean value of three replicate samples and corresponding standard deviation.

## SERS-DAHS method detection of Real Sample

To further test the performance of the method introduced here, SERS-DAHS was employed in the on-site detection of aromatic pollutants in real printing and dyeing wastewater provided by Modern Dyestuffs & Pigments Co., Ltd. in Ningbo, China. FPAPs were mixed with three real wastewater samples respectively and then separated through a solid-liquid hydrocyclone after the adsorption process was complete. SERS spectra of the pollutants on the surface of FPAPs (Figure 5C) were recorded after FPAPs were dried under nitrogen as described above. Through comparison with the calibration curve library and the log-log curves above (Figure 3 and Figure 4E-G), benzidine, aniline, and parachloroaniline were identified on the surface of FPAPs. The corresponding quantities of pollutants adsorbed on 1 kg of FPAPs were determined to be 20.5 mg/kg, 92.7 mg/kg and 40.9 mg/kg respectively (Figure 5D). As a control, aliquots of the assayed wastewater samples before and after DAHS were also analyzed using GC-MS (Shimadzu QP-2010, Japan). benzidine, aniline and parachloroaniline were also detected in the samples (Figure 5A-B) using GC-MS, in amounts of 18.8mg/kg, 98mg/kg and 47mg/kg respectively (Figure 5D). Comparison of the results obtained from the two methods demonstrates that the detection performance of the straightforward and simple SERS-DAHS method is similar to that of the more complex GC-MS technique for detection of aromatic compounds, with detection results deviating by no more than 10% between these two techniques.

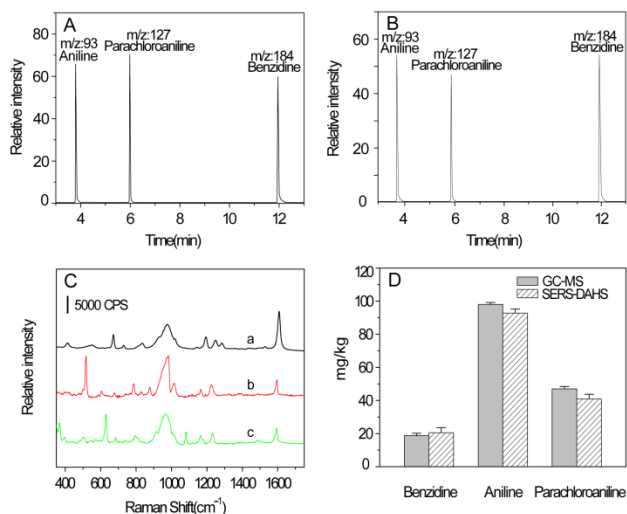


Figure 5 GC-MS spectrum of the real sample (A) before and (B) after DAHS; (C) SERS spectra of the detected pollutants: (a) benzidine, (b) aniline, (c) parachloroaniline; (D) Comparison of the quantitative detection results between SERS-DAHS and GC-MS. Error bars represent the mean value of three replicate samples and corresponding standard deviation.

## Conclusions

The present work demonstrates that the SERS-DAHS technique is an excellent candidate for the qualitative and quantitative detection of aromatic compounds on the surface of single particle, and that the analytical ability of this method is

comparable to that of traditional techniques such as GC-MS. More importantly, SERS-DAHS is preferable for direct detection of pollutants adsorbed on porous materials and shortens detection time considerably, thereby providing a valuable technique for on-site quantitative analysis of aromatic compounds/pollutants on the surface of particle directly.

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## Notes and references

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