Quantitative determination of airborne redox-active compounds based on heating induced reduction of gold nanoparticles

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Abstract
Airborne redox-active compounds (ARC) account for a substantial fraction of atmospheric aerosols and play a vital role in chemical processes that influence global climate, human and ecological health. With the exception of the determination of total organic carbon by the expensive Total Organic Carbon (TOC) analyser, there is currently no easy-to-use method to quantify ARC. Here we designed a method to detect the concentration of ARC by using the thermal-induced reduction and colorimetric behaviours of gold nanoparticles (AuNPs), in which the humic substances (HS) was used as standard model of ARC to calculate the HS-equivalent concentration of ARC. Distinguished from the conventional complex methods, e.g., TOC analysis, the proposed approach measured localized surface plasmon resonance (LSPR) absorption of AuNPs and the target ARC concentration can be either directly quantified by the absorption spectrometer or qualitatively evaluated by the naked eyes. By using the absorption spectrometer, a limit of detection (LOD) of 0.005 ppm by our AuNP sensor was achieved. To validate this sensing technique, aerosol samples collected from Basel (suburban), Bern (urban), and Rigi mountain (rural and high-altitude) sites in Switzerland were further investigated through the TOC combustion method. The results thereby substantiated that our plasmonic absorption-based AuNP sensor upholds a great promise for fast, cost-efficient total ARC detection and air quality assessment.

This document is the accepted manuscript version of the following article: Yu, R., Pan, F., Schreiner, C., Wang, X., Bell, D. M., Qiu, G., & Wang, J. (2021). Quantitative determination of airborne redox-active compounds based on heating-induced reduction of gold nanoparticles. Analytical Chemistry, 93(44), 14859-14868. https://doi.org/10.1021/acs.analchem.1c03823
**Introduction**

Airborne redox-active compounds (ARC) account for a substantial fraction of atmospheric aerosols, which could be generated by a variety of sources\(^1\),\(^2\) including vehicular emissions, biomass burning, industrial exhaust, negatively impacting on global climate change and displaying damage on health.\(^3\) The water-soluble organic carbon (WSOC) and transition metals\(^4\) are recognized as the main components of ARC\(^5\). According to the literature,\(^6\),\(^7\) humic-like substances in WSOC and some transitional metals (e.g., Fe\(^{2+}\)) have both the electron accepting capacities and electron donating capacities. For instance, quinones in WSOC can catalyze electron transfer due to their ability to form stable semiquinone radicals. Semiquinone radicals can obtain electrons from reductants and donate electrons to oxidants.\(^8\) Therefore, ARC have a high oxidative potential to generate reactive oxygen species (ROS) in the human respiratory tract, responsible for further oxidative stress and airway inflammation.\(^9\),\(^10\) Moreover, it is confirmed that WSOC\(^11\) have a great influence on hygroscopicity and cloud condensation nuclei (CCN) ability. Quantitative and qualitative analysis of ARC is thus highly crucial for understanding and assessing its influence on air quality, ecological health and global climate.

Currently, numerous analytical methods have been applied for qualitative and quantitative analysis of the airborne organic compounds. For qualitative analysis, fluorescence spectroscopy,\(^12\) Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS),\(^13\) gas chromatography-mass spectrometry (GC-MS),\(^14\) nuclear magnetic resonance (NMR),\(^15\) high-resolution time-of-flight aerosol mass spectrometry (HR-TOF-AMS)\(^16\) are developed for analysing molecular weight range and functional group compositions. Many studies found some compounds in aerosols had similar physical and chemical properties to naturally occurring HS, such as acidity, light absorption ability, fluorescence spectra and FT-IR spectra.\(^17\),\(^18\) They generally hold very similar carbon functional groups.\(^19\) These types of functional groups such as phenol, carboxyl group, ketone and aldehydes can act as reducing sites for metal ions. Humic acid (insoluble at low pH) and fulvic acid (soluble at all pH) are the predominant components of HS. These two compounds are thus often used as models of WSOC.\(^20\),\(^21\)

For quantitative organic species analysis, two types of carbon analysers, \textit{i.e.} total organic carbon (TOC) analyzer and aerosol carbon analyzers (ACA) are widely used.\(^22\) The quantification principle of these two methods is based on the conversion of carbon compounds into CO\(_2\) and the detection of CO\(_2\) concentration after pre-treatment.
Generally, ACA requires extensive manual operation while TOC quantification requires estimating the concentration before the test. Moreover, these techniques require trained operators and sophisticated processes like laborious pre-treatment. Furthermore, pre-treatment of atmospheric samples often leads to loss of organic species, especially those with lower solubility after acidification. When using these methods to evaluate the redox activity, only the organic components are considered, while the inorganic metal ions or complexes of metals and organics are ignored. Therefore, the development of sensor that could be easily and routinely used for detecting ARC is a big step forward.

The recent progress about metal-engineered nanomaterials has attracted extensive interests in new analytical assays that demonstrated high sensitivity, rapidity of analysis and easy-to-process signals perceptible even by naked eyes. Noble metal nanoparticles, especially those made by gold and silver, demonstrated an enhanced light-matter interaction and intense absorption band in the visible region. This strong LSPR absorption at specific resonance frequency is highly dependent on the particle size, shape, geometry, inter-particle distance, as well as refractive index of media. Any changes in these parameters may affect LSPR frequency and result in a shifting of the absorption. Based on this principle, various sensors relying on AuNPs have been developed and applied in heavy metal detection, DNA and protein discrimination. Of particular interest is the colorimetric sensors, which have been widely applied for the determination of many analytes upon measuring the changes in absorbance and colour.

AuNPs could be obtained by many preparation routes such as in situ chemical reduction, seeded growth, vapor deposition and pulse radiolysis. The green-chemistry reduction is one of the promising method because of eco-friendly reactants. Natural organic matter (NOM) such as plants extracts, microorganisms or other organic compounds have been found to have redox behaviour and can be used in the synthesis of highly stable AuNPs. NOM are ubiquitous occurring in soil, sediments, aquatic and atmospheric environment, which served as one of the important sources of ARC. The phenolic, aldehyde and alcoholic groups in NOM are considered to be capable of complexation and reduction of metal ions. In addition, some researchers suggested quinone/hydroquinone moieties in NOM were the candidates for electron transfer in the
redox process and reduce metal ions to metal nanoparticles. Moreover, NOM can stabilize and disperse AuNPs serving as a coating agent. Despite many investigations about interaction between Au ions and redox-active NOM in aquatic environment, few studies focus on the interaction between Au ions and ARC.

In this work, we propose a simple, fast and cost-effective ARC quantification method based on the electron donating ability of ARC and LSPR colorimetric response of reduced AuNPs. We chose humic acid (HA) and Suwanee river fulvic acid (SRFA) as ARC models. The absorbance intensity of AuNPs was in linear relationship both with the concentration of HA and SRFA. The ARC concentration in the environmental samples was determined by measuring the absorbance intensity of AuNPs or using naked eyes without resorting to any complex or expensive analytical instrument. This proposed assay gave rise to an easy-to-use and one-step method. Furthermore, the proposed assay was applied to study different real aerosol samples and the results were verified by using standard airborne carbon compounds quantification method. To the best of our knowledge, our work is the first direct quantification of ARC by using AuNP-reduction method. Our proposed method combined the green-chemistry reduction ability of ARC and the sensitive colorimetric response of AuNPs, which provided an easy-to-use analytical method for on-site and fast environment assessment.

Experiment section

Procedures for ARC quantification

Typically, the reactant mixture of 4.75 ml target sample (eg. HA, SRFA or real atmospheric samples), 197 µl 25.4 mM aqueous HAuCl₄, 40 µl 0.5 M NaOH and 13 µl deionized water was heated in an oil bath at 100 °C for 40 minutes. The total volume was set as 5ml. HA solution was dissolved in distilled water with pH adjusted to 8-9 by NaOH to assist solubility. To obtain the maximum colorimetric response, the reaction conditions including pH, HAuCl₄ concentration and temperature were optimized. Information about reagents and characterization AuNPs is shown in S1 and S2 of the SI.

Aerosol sampling, collection and preparation.

Aerosol sampling was carried out at three sites of Swiss National Air Pollution Monitoring Network (NABEL). The monthly specimens were from Bern (Bollwerk, an urban area), Basel (Binningen, a suburban area), and Rigi (Seebodenalp, a rural area)
Validation test with TOC analyzer

ARC in environmental samples can be quantified based on the calibration curve of HS and identified as an HS-equivalent concentration. HS-equivalent concentration measurement was also carried out with a TOC analyzer (Shimadzu TOC-L) to testify the sensor validity. Details are shown in S4 of the SI.

Results and Discussion

ARC-mediated AuNPs reduction

The ARC-mediated reduction process is depicted in Scheme 1. The determination of ARC was achieved by measuring the absorbance intensity of the reduced AuNPs. As shown in Figure S1, the FTIR bands at 1715 cm\(^{-1}\) can be attributed to the C=O carboxyl and ketonic carbonyl \(^{24,37}\) which can act as reduction site. Furthermore, we found that the band at 1715 cm\(^{-1}\) for SRFA is stronger than that for HA. This further proved that the SRFA has a higher carboxyl content and a higher solubility in water. Considering the standard redox potentials of reactants (0.780 V and 0.5 V for HA and SRFA \(^{38,39}\) while 1.002 V for Au\(^{3+}\) in acid condition\(^{40}\)), the reduction reaction can naturally occur at room temperature, while the heating will accelerate reaction rate. The HA and SRFA possess similar carbon functional groups as ARC and may co-exist in real samples with various proportions, therefore, HA and SRFA were chosen as the ARC models in this work.

Optimization of reaction conditions

The LSPR sensing performance was dictated by the physiochemical properties of AuNPs. To achieve a strong and reproducible response, we optimized the experimental conditions by adjusting pH, aqueous HAuCl\(_4\) concentration and temperature. The pH value in the reaction system played a major role on the yield, size and shape of AuNPs. NaOH was used to tune pH values and ionic environment of the reaction solution. Figure 1a and 1b depicted the absorption spectra of HA-mediated and SRFA-mediated AuNPs with different NaOH concentrations, which demonstrated the variability of the AuNPs concentration and size. We found that the maximum absorption band in the absence of NaOH (pH 3.57) lied in higher wavelengths indicating the formation of larger particles and the reduction rate is much lower. The low pH might lower the quinone redox reactivity in HS, which resulted in lower reduction rate.\(^{41}\) Moreover, the AuNP colloid solution reduced by HA and SRFA in the absence of alkali (acid
condition) were less stable and easy to agglomerate and precipitate. Triangle, rod-like and other irregular polygonal shaped AuNPs reduced by SRFA were shown in the TEM image (Figure S2) and a yellow sediment appeared at the bottom of the reaction chamber (Figure S3). With the increased alkaline concentration (pH increased from 5.73 to 11.17), we observed a relatively higher reduction rate as well as a narrower absorption band and blue-shifted peak wavelength (Figure S4), which indicated the formation of more monodisperse and smaller NPs. These results were verified by TEM imaging given in Figure 1d and Figure S2. Higher pH value was favourable for the formation of AuNPs as the redox potential ($E_h$) of HS decreased with the increased pH.39,42 Reducing groups including carboxylic and phenolic groups at higher pH were ionized, generating higher electric negative charge to stabilize the growing AuNPs.43,44 In this sense, we got smaller and more stable AuNPs at high pH value. Furthermore, we investigated the colorimetric properties of HA- and SRFA-reduced AuNPs at different pH values (Figure S4 and 1c). HA yielded much higher intensity and larger AuNPs compared to SRHA. According to previous literature, natural organic matter with high aromatic content but low aliphatic-carbon contents has a higher reactivity to reduce Au$^{3+}$.45 HA has higher aromatic carbon content than SRFA.46 Therefore, HA produced more intense signal than SRFA. Since HA had lower density of carboxylic and phenolic groups than SRFA46, HA provided less interaction sites to stabilize AuNPs and yield larger AuNPs. Reduction of aqueous HAuCl$_4$ by HS also caused a decrease in pH value as seen from Figure S5, indicating the alkali might participate the reduction reaction. This had a good agreement with the previous work.47 It is worth noting that pH also has a significant impact on the reaction of Au precursor. Under the alkaline condition with high pH, Au precursor transformed from AuCl$_4^-$ ($E_h$=1.00 V) to Au(OH)$_4^-$ ($E_h$=0.60 V),40 which indicated that the reduction of Au(III) to Au would be favourable at lower pH. Due to the competition between the pH-dependent impact of Au (OH)$_4^-$ and $E_h$ of HS, the reduction rate first increased and then decreased with the increasing pH.33 With comprehensive consideration of the impact on the absorption intensity, AuNPs stability and reaction rate, 4 mM NaOH and 1mM HAuCl$_4$ (with final pH equaling 10) were chosen as the optimum. The effect of HAuCl$_4$ concentration on the formation of AuNPs was further evaluated under the fixed pH (10). Figure S6 and Figure S7a shows that the elevated HAuCl$_4$ concentration facilitated the AuNP formation and increased the corresponding absorption intensity. The position of maximum absorption shifted to higher wavelength
with the increased HAuCl₄ concentration, indicating the formation of larger AuNPs at higher HAuCl₄ concentration (Figure S7b). This result was in accordance with that measured by DLS. This implied that higher HAuCl₄ concentration was beneficial for the further growth of AuNPs. But for concentration of HAuCl₄ above 1 mM in the case of HA or above 2.5 mM in the case of SRFA, the absorption intensity declined and AuNPs began to precipitate. According to TEM images (Figure S8), the concentration of HAuCl₄ had no significant impact on the final size and morphology of the SRFA-reduced AuNPs when the concentration was below 3 mM. While above 3 mM HAuCl₄, the SRFA-reduced AuNPs linked together and aggregated to worm-like particles. In order to make sufficient reaction of HS and keep stability of colloidal solution, 1 mM HAuCl₄ was finally applied.

Temperature is another controlling factor for heating-induced Au reduction. At room temperature (RT), no obvious absorption peak of AuNPs reduced by HA were observed even after 5 days while the absorption peak of AuNPs was observed after incubation with SRFA (Figure S9). Under the elevated temperature, the formation rate of AuNPs increased significantly. Higher temperature accelerated the reduction rates of Au(III) and shortened the reaction time. Therefore, we decided to conduct the test at 100 °C. Furthermore, in order to get real-time reaction dynamics, time-resolved absorption of AuNPs at a concentration of 1 ppm for HS was investigated. Figure S10 showed that the absorbance intensity reached steady and the colour did not change after 35 min. Hence, we set the total reaction time as 40 min.

**Calibration and analytical figures of merit**

Herein the concentration-dependent reduction of AuNPs was investigated with HA and SRFA. The standard HS solutions with concentrations ranging from 5 ppb to 100 ppm were analysed, and the absorption spectra were consequently depicted in Figure 2a and 2b. The blank sample (HAuCl₄ and NaOH solution) was used as the reference for evaluating LOD and LOQ (limits of quantification). The detailed calculating method were provided in the Supporting Information S5 and Table S2. For the blank samples, the mean absorbance intensity was 0.0102 with the standard deviation of 0.00466. By increasing the concentration of HS, the maximum absorbance intensity of AuNPs rose, and the peak of the maximum absorbance shifted to a shorter wavelength. Moreover, SRFA produced comparatively smaller diameter of AuNPs than HA as shown in Figure
Subsequently, the regression relationship was further studied with 12 different HA and SRFA samples. HA and SRFA both demonstrated satisfactory correlation between the HS concentrations and absorbance intensity. Details are shown in Table S1. The linear-regression fitting was in the range from 100 ppm to 1 ppm and 1 ppm to 5 ppb. More importantly, a similar response for HA and SRFA was noticed as shown in Figure S11. Therefore, the absorption responses of HA and SRFA data were integrated into a single calibration curve as shown in Figure 2d. The fitting of the calibration graph generated a reference regression equation: 

\[ y = 0.01657x + 0.06903 \quad (x \geq 1\text{ ppm}), \quad R^2=0.99; \]

\[ y = 0.05364x + 0.03077 \quad (x < 1\text{ ppm}), \quad R^2=0.96. \]

According to S5 and Figure S11c, the LOD and LOQ was determined to be 0.005 ppm and 0.5 ppm, respectively. We can also visually distinguish the colours of the blank measurement and the AuNPs solution reduced by low-concentration (0.005 ppm) SRFA as shown in Figure S11d. Compared to the conventional TOC method (LOD: 0.05 ppm), the proposed AuNP sensors exhibited a lower LOD. It is also found that the colour of the reaction solution gradually changed from pale pink to dark wine-red with the increasing HS concentration. We can thereby qualitatively determine the presence of HS and evaluate the sample concentration by naked eyes.

**Analysis of real-world environmental samples**

In order to evaluate the feasibility of the AuNP sensor, 36 aerosol samples collected from three typical environment over 12 months were detected and triplicate measurements were conducted for each sample. The measured absorbance as shown in Figure S12 was applied in the regression equation to evaluate the HS-equivalent concentration in each monthly sample. Although the environment samples were complex and different from HA and SRFA, both the collected filter samples and HA/SRFA possessed similar reducing sites for the formation of AuNPs. As shown in Figure 3a, for the suburban sites in Basel, HS-equivalent concentration was found in the range of 1.3 \( \mu \text{g}\cdot\text{m}^{-3} \) to 150 \( \mu \text{g}\cdot\text{m}^{-3} \). The highest was found in January while the lowest was in July. For the urban roadside in Bern (Figure 3b), the concentration ranged from 2.8 \( \mu \text{g}\cdot\text{m}^{-3} \) in July to 127 \( \mu \text{g}\cdot\text{m}^{-3} \) in January. As a high-altitude and low human activity region, Rigi mountain (Figure 3c) showed the HS-equivalent concentration within a low-level range from 1.2 \( \mu \text{g}\cdot\text{m}^{-3} \) in October to 31.3 \( \mu \text{g}\cdot\text{m}^{-3} \) in August.
Comparing the urban and suburban stations, high-altitude region exhibited a relatively low and steady HS-equivalent concentration.

From the perspective of seasonal distribution as shown in Figure 3d, the content of ARC showed a clear geographical and seasonal variation with elevated concentrations in the cold period of the year (117.3 µg·m⁻³ in winter and 70.9 µg·m⁻³ in fall) and reduced levels in the warm time of the year (24.9 µg·m⁻³ in spring and 4.2 µg·m⁻³ in summer) for the suburban environment in Basel. For the urban environment in Bern, they showed similarly higher values during winter (60.1 µg·m⁻³) and fall (30.6 µg·m⁻³) and lower values in spring (14 µg·m⁻³) and summer (6.7 µg·m⁻³). These values agreed with previously reported ROS measurements from Daellenbach et al.¹ (2021) where winter-time samples showed enhanced ROS formation. Using size-segregated analysis they showed during the winter season in the fine mode, ROS activity was dominated by anthropogenic SOA from residential biomass burning, while in the coarse mode, it was dominated by metals from vehicular non-exhaust emissions (e.g. tyre wear). In the measurements presented here, PM10 filter samples are being used so they possess both the anthropogenic SOA and the non-exhaust emissions from cars found in the coarse mode. Overall, these seasonal variations resulted from weather conditions (lower boundary layer) and the seasonality of the SOA present². The high HS-equivalent concentrations were associated with large amount of biomass burning emissions and slow degradation rate in the cold seasons. However, the strong convective activity in summer lead to air pollutants diffusing.⁴⁸ In contrast to the urban area, the seasonal trend in the rural and high-altitude station showed higher concentrations of HS-equivalent in spring (9.35 µg·m⁻³) and summer (20.36 µg·m⁻³) and lower concentrations in fall (2.2 µg·m⁻³) and winter (6.2 µg·m⁻³). Additionally, Rigi mountain showed a lower-level HS-equivalent concentration in cold seasons than the urban and suburban stations. This was associated with the high altitude, sparse population and minimal industry activity. Similar seasonal variations in high-altitude region to our observations have been reported by Xu et al. for Tibetan Plateau in China⁴⁹ and Hegde & Kawamura⁵⁰ for Himalayas in India. The results from these three sites demonstrate that the HS-equivalent concentration has geographical and seasonal variability due to the different origins of aerosols.

Furthermore, we investigated AuNPs formed by environmental and standard samples using comprehensive characterizations including STEM, TEM, EDS and SAED. The
STEM and TEM images (Figures 4a-1, b-1, c-1, d-1 and Figure S13) demonstrated that
the most AuNPs were sphere-like. The SAED patterns as shown in Figures 4a-2, b-2,
c-2, d-2 demonstrated the same diffraction rings of gold obtained from environmental
and standard samples. From inner to outer, the rings correspond to (111), (200), (220),
and (311) reflections, revealing a crystalline face-centered cubic (fcc) lattice structure.
The EDS spectra shown in Figures 4a-3, b-3, c-3, d-3 further confirmed that the
particles in TEM images were AuNPs. In addition, we found that the size of AuNPs
formed by environmental samples were similar with those formed by HA but larger
than SRFA (Figure S14). In summary, the UV-vis, TEM, STEM, SAED, EDS results
provided conclusive indication of the formation of AuNPs regardless of the type of
sample used. Therefore, our AuNP reduction sensing method can be applied in
analysing different environmental samples containing the redox-active compounds.

Validation of the Sensor

To further validate the proposed method, the HS-equivalent concentrations of the
samples were tested by TOC combustion method. We first prepared standard samples
concentrations ranging from 1 ppm to 70 ppm and tested their TOC concentration. As
shown in Figure 5a, the TOC concentration of HA and SRFA measured by the TOC
analyser showed strong correlation with HS mass concentration, that is,
\[ y_{HA}=0.33357x+0.6047, \quad R^2_{HA}=0.999; \quad y_{SRFA}=0.48374x+0.78322, \quad R^2_{SRFA}=0.997. \]
The intercept might be caused by the blank contribution. We also found that the
concentration accounted for less than half of the mass concentration of standard
samples from the fitting correlations (33% in HA and 48% in SRFA). Furthermore,
TOC measurements of 15 environmental samples were also obtained as shown in
Figure 5b. A strong correlation (R^2=0.945) between the TOC concentration and HS-
equivalent concentration measured by the AuNP sensor was observed. This result
demonstrated that the sensor signals correlated well with the TOC measurement, which
indicated the applicability of the proposed AuNP sensor. However, the HS-equivalent
concentration quantified by the current method was one order higher than that of TOC
combustion results.

Worthy of note, the TOC method only measured the amount of total carbon in the
analytes rather than the total mass of compounds, since a non-negligible portion of the
mass comes from other oxygen containing functional groups.\(^{18}\) Therefore, redox-active
organic compounds should be estimated by multiplying the TOC concentration with a
conversion factor. But the conversion factor is uncertain due to the different origins of aerosols and different treatment methods. Moreover, pre-treatment before the TOC analysis, such as acidification with addition of HCl would lead to the loss of organic species due to the deceased solubility. These losses agreed well the previous work, where dissolved organic carbon concentrations in freshwater samples and HA samples by TOC measurements decreased by 4–12% and 17%, respectively. Therefore, the TOC analyser detected an even lower fraction of HA than that of SRFA, as HA was less soluble under acidic condition.

Our sensor is based on redox reaction method to evaluate ARC mass content for participating the AuNP reduction, not just carbon-containing organic species concentration. As for the measured ARC concentration higher than the PM10 concentration, there may be two main reasons. First of all, atmospheric WSOC can be separated into hydrophobic and hydrophilic fractions using solid phase extraction. The hydrophobic fraction holds similar carbon functional groups as HS. The phenolic, alcoholic, and aldehyde groups in HS are assumed to serve as reduction sites during the reduction processes. Some studies declared that superoxide free radicals (O$_2^-$, associated with the phenolic group$^{31,33}$ in HS) or other intermediates (including hydrated electrons and excited triplet) formed by HS may participate in the reduction of metal ions$^{31,53}$. Meanwhile, previous work suggested that quinone/ hydroquinone are major reducible moieties in HS$^{34,35}$. Therefore, the hydrophobic portion of WSOC facilitate the reduction of AuNPs. Additionally, many hydrophilic compounds such as monocarboxylic acid: formic acid$^{54}$; dicarboxylic acid: oxalic acid$^{55}$ and succinic acid$^{56}$; saccharides: sucrose$^{57}$; amines$^{58}$; amino acids$^{59}$ also have abilities to reduce aqueous HAUCl$_4$ and increase AuNP absorbance intensity. For example, citric acid with smaller molecular weight$^{60}$ as one of water-soluble organic acid in hydrophilic fraction can reduce Au$^{3+}$ and get higher intensity compared to HS as seen in our verification experiment in SI Figure S15. Moreover, previous work has substantiated that a significant contribution (36%) of water-soluble organic matter to generate superoxide radials was ascribed to hydrophilic fraction.$^5$

Secondly, the major components of redox-active species in aerosols are thought to be transition metals$^{61}$ and quinones which have been identified to be one type of redox
sites in atmospheric humic-like substances (HULIS). Iron as one of most abundant transition metals ranging from 0.09-1152 ng.m\(^{-3}\) in PM suspensions across the Europe\(^{62}\) plays a vital role in redox recycling. Fe(II) not only acts as a green reducing agent\(^{63}\) in synthesis of AuNPs, but also can react with oxygen to generate O\(_2^-\), which might be responsible for Au(III) reduction. Additionally, HULIS have abilities to bind with Fe (II) through organic-metal complexation and enhance the hydroxyl radical formation.\(^{64,65}\) Hydroxyl radical can form H\(_2\)O\(_2\) which is a another green reducing agent for Au(III) reduction.\(^{66}\) It is also interesting to note that dicarboxylic acid such as oxalic acid can also increase the solubility of Fe by metal-ligand complexation.\(^{67}\) It is worth noting that Mn(II)\(^{68}\) and Al(III)\(^{69}\) were both found to reduce Au(III) in alkaline condition. These airborne components or organic-metal complexes exhibited a higher reduction ability than the model HS, therefore the HS-equivalent concentration measured by our sensor were higher than that by TOC analyser, and even surpass the mass of PM10. Although the absolute value might surpass the total mass of PM, this HS-equivalent concentration level can be a reliable indicator for fast comparison of the redox capability in different environmental aerosols.

**Conclusions**

We have for the first time achieved the direct quantification of atmospheric ARC concentration based on the combination of reduction ability of the ARC and colorimetric characterization of the AuNPs. The AuNP sensor was initially calibrated with two standard ARC substances, *i.e.* HA and SRFA, therefore the ARC can be quantified as an HS-equivalent concentration based on the integrated calibration curve. Particularly of interest, the colorimetric responses of the ARC can be evaluated by either measuring AuNPs absorbance with standard facilities, or by direct visual inspection. In our preliminary validation tests, atmospheric samples from three different environmental scenarios demonstrate the colorimetric results reported by the AuNP sensor had a strong correlation with that of standard TOC tests, which not only confirmed the validity of our proposed AuNP sensor, but also indicated that the ARC was one of the dominating components in airborne organic matter. Furthermore, this method outperformed the standard TOC measurement regarding the LOD, efficiency, flexibility, simplicity for routine ARC detection. Especially, this rapid and simple method, based on the redox potential of compounds is universal and not exclusive to
ARC. We believe that this method is applicable to other complex systems such as dissolved organic matter in aquatic environment readily.

ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge at https://pubs.acs.org.

- Additional experimental methodologies, details on HS and reduced AuNP characterizations, experiment optimization and sensing performance.

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Notes

The authors declare no competing financial interest.

Acknowledgments

Ranxue Yu thanks China Scholarship Council and Donghua University for the financial support. She also thanks the National Natural Science Foundation of China (Grant Nos. 51776034) for the support.

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Scheme 1. Schematic of ARC-mediated reduction process.
Figure 1. Effect of NaOH concentration on the absorption of AuNPs by (a) HA and (b) SRFA and (c) AuNPs size, (d) TEM image of the AuNPs using SRFA containing 4mM NaOH. Reduction condition: c(HS)=100 mg:L⁻¹, c(HAuCl₄) =1mM, c(NaOH) = 0-8mM, T=100ºC, t=40min.
Figure 2. Optical absorption spectra of AuNPs formed by (a) HA and (b) SRFA. (c) AuNPs size formed by HA and SRFA ranging from 1ppm to 100ppm. (d) A calibration curve combining SRFA and HA based on absorption spectra of AuNPs.
Figure 3. Comparision monthly HS-equivalent concentration at (a) Basel, (b) Bern, (c) Rigi Montain and (d) seasonal concentrations at Basel, Bern, Rigi Montain. The error bars represent the standard deviations for three replicates.

Figure 4. STEM images, SAED, the corresponding EDS of AuNPs in (a) Basel in January, (b) Bern in January, (c) Rigi in July and (d) 10ppm SRFA.
Figure 5. (a) Linear fitting between the TOC concentrations and mass concentrations of HA and SRFA determined by dilution of the stock solutions, (b) Linear fitting between the TOC concentrations and HS-equivalent concentrations measured by AuNP sensor for real-world environmental samples in Basel, Bern, Rigi Mountain.