Analytical Methods

PAPER

Sensitive and simple sonoluminescent detection of melamine via aggregation of Au nanoparticles

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In this work, we reported a novel Au nanoparticles-sonoluminescent (AuNPs-SL) design for simple and high throughput detection of melamine with a lab-made SL vial. Aqueous SL at 520 nm can be sensitively quenched and restored by dispersed and aggregated AuNPs, respectively. Based on it, the melamine resultant aggregation state of AuNPs is characterized by measuring the SL variation, as well as 10 the content of melamine. All the ultrsound parameters and experimental variables, including the ultrasound irradiation duration and interval, the test solution composition, the melamine-AuNPs interaction time, were separately investigated and optimized. The established SL method exhibits good linear SL response to melamine concentrations in the range from 10 to 240 nM with a limit of detection (3σ) of 3 nM. The proposed method has been applied to quantification of melamine in milk products. 15 Statistical analysis results from F and t tests demonstrated the agreement between SL method and official method both in precision and accuracy.

Introduction

Melamine (1,3,5-triazine-2,4,6-triamine) is a chemical compound commonly used in the synthesis of melamine formaldehyde resins 20 and medical materials. Normally, melamine can be found at ppm levels in foods and beverages because of the degradation of melamine-containing resins[1] or cyromazine.[2] Safety limits of melamine have been officially set to be 1 ppm for infant formula in China and 2.5 ppm in the United States and European Union 25 for foods.[3,4] It has been demonstrated that excessive uptake of melamine causes the formation of insoluble melamine cyanurate stones in the kidney, which induce urinary calculus, renal dysfunction and even death.[5] Melamine resultant cyanurate stones are also suspected to cause bladder cancer.[6,7] In recent years, 30 melamine has been found illegally added to dairy products and animal foods with the aim to increase the apparent protein content due to its high nitrogen level of about 66% by mass. Conventional Kjeldahl test cannot recognize nitrogen source in principle when applied to protein analysis, and hence, gives false 35 results. Consequently, developments of selective, sensitive and reliable methods that can detect melamine at ppm level or lower are of considerable significance.

Reported techniques for melamine analysis mainly include liquid chromatography,[8] gas/liquid chromatography-mass 40 spectrometry,[9,10] electrochemical methods,[11,12] nuclear magnetic resonance spectroscopy,[13] enzyme-linked immune-sorbent assay,[6,14] and surface enhanced Raman spectroscopy.[15] However, most of the above approaches require relatively expensive instrumentation and complicated analytical procedures. 45 Therefore, simple and low-cost techniques without the need of costly instrumentation and pre-concentration are expected. More recently, nano-materials have been introduced for melamine analysis,[16-21] in particular gold nanoparticle (AuNP) for its unique optical properties. Based on the interaction between melamine 50 and AuNPs which provokes the formation of aggregates and induces the surface plasmon resonance (SPR) shift with the color change from red to blue, UV/Vis detection and even naked-eye inspection methods have been developed.[22-24] In addition, AuNPs aggregation-caused property changes in light scattering allowed 55 the development of dynamic light scattering and surface enhanced Raman scattering methods for sensitive melamine detection.[25,26] By taking advantage of the extremely quenching ability of AuNPs (10^8-10^{10} M^{-1} cm^{-1} extinction coefficients for 13-18 nm AuNPs at 520 nm),[27,28] highly sensitive and selective 60 melamine analysis was realized through the fluorescence energy transfer principle.[29,30] The advantage of utilizing AuNPs for sensitive melamine recognition has been extensively exhibited.

Sonoluminescence (SL) is the emission of short bursts of light from collapsing bubbles when a liquid is irradiated by ultrasound 65 power. It is estimated that, during bubble collapse, the high temperature up to 10000 and even 100000 kelvins in the interior of the bubble results in atom ionization and consequent light emission. In air saturated water, the SL spectrum is proved featureless extending over the wavelength region from 200 nm to 70 800 nm.[31-32] That is, SL can be an available endogenous light source. SL detection has been proved the advantages of simple,

low-cost and robust device.[33] However, SL researches specified for quantitative chemical detection are rare to be found,[31,33-34] the capability of SL has not yet been well explored. Encouraged by the success of nano-materials enabled sensitive molecule recognition and the attractive device of SL, the goal of this work is to develop a new design of nano-material and SL integrated analysis. With the known size-dependent SPR of AuNPs, it is presumed that by measuring the SL variation at a certain wavelength, for example 520 nm, the aggregation state of AuNPs

can be characterized. As such, an analyte which may induce AuNPs aggregation can be detected by SL. Our experiments found that the quenched SL at 520 nm by 13 nm dispersing AuNPs can be restored in presence of melamine. Based on it, an AuNPs-SL method was developed for sensitive and quantitative melamine analysis. Its feasibility and reliability have been validated by comparing the SL results with those from official method (Chinese standard GB/T 22388-2008) for milk products.
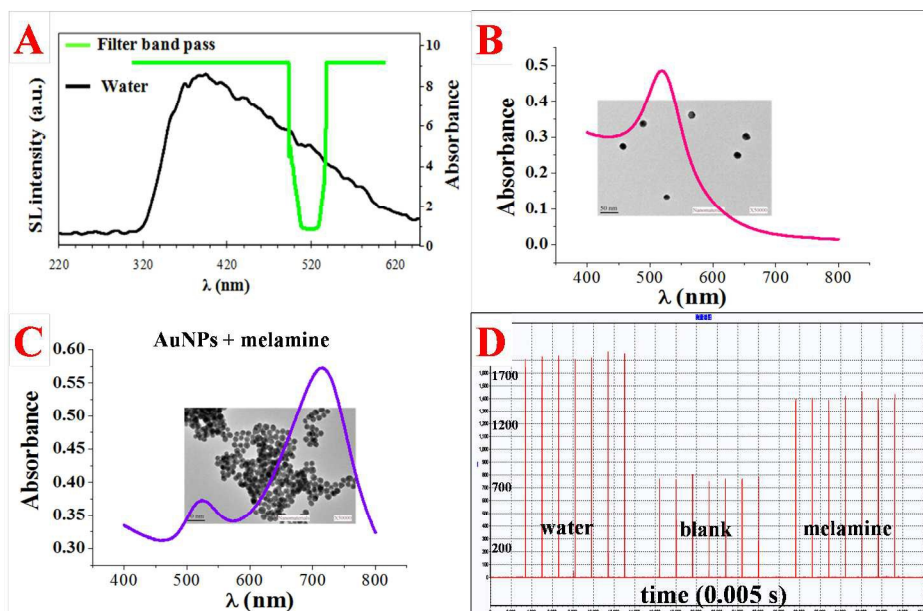
Fig.1 Principle of our AuNPs-SL detection for melamine. (A), the SL spectrum of water and the band pass of interference filter represented as the UV/Vis absorption spectrum; (B), the UV/Vis absorption spectrum of 13 nm AuNPs peaking at 520 nM and the TEM image to validate the dispersed state of AuNPs; (C), the UV/Vis absorption spectrum of 1.0 μM melamine resultant aggregated AuNPs and the TEM image validate the aggregation state of AuNPs; (D), the SL responses with respect to inserts of (A), (B) and (C) labeled as water (0.21 mM sodium citrate), blank, melamine, respectively.

Experimental

Chemicals and reagents

All chemical reagents used are of analytical grade unless otherwise indicated. $HAuCl_4$ was purchased from Shanghai Chemical Reagent Co., Ltd (China). Sodium citrate, melamine, ethyl acetate and citric acid were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Acetonitrile, methanol and sodium n-heptanesulfonate (chromatographic grade) were obtained from Oceanpak Company (Sweden). Deionized distilled water was used throughout the experiments. Milk products were purchased from local supermarket in Xi'an city.

AuNPs (13 nm in diameter) were synthesized through the reduction of $HAuCl_4$ by sodium citrate according to the literature.[22] Typically, 0.72 mL 1% sodium citrate was rapidly added into 20 mL 0.01 % boiling $HAuCl_4$ solution with vigorous string. The mixed solution was kept boiling for 10 min into red wine suspension. Then, the suspension gradually cooled to room temperature under string. Finally, the synthesized colloidal gold nanoparticles were stored in a refrigerator at 4℃ before use.

Apparatus

The schematic diagram of the lab-made SL vial and the system are showed in Fig. S1. A ceramic flat-plate transducer (Annon

Piezo Technology Co., Ltd., Shenzhen, China) was attached to the bottom of a 15 mL bottomless glass vial. The transducer is driven by the function generator of a home-used humidifier with the acoustic frequency (1.73 MHz). An ATR02-S time controller (Shanghai Zhuo-yi Electron Co., Ltd., China), which commands the function generator, is used to control the irradiating duration and interval. Three teflon tubes were set into the SL vial through a rubber cover for sample loading, waste removing, and pressure balancing, respectively. The SL vial was enwrapped with a glistening Aluminium-foil to collect SL to the photo multiplier tube (PMT, R647-04 Hamamatsu Japan) through a 1 cm width exit. A 520±15 nm band pass interference filter (Shenzhen Jiante Spectra Co., Ltd., China) was arranged between the SL exit and the PMT window to obtain 520 nm SL signal. Two 10 mL syringes were used for sample loading and waste removing, respectively. Powered at -700 V, the PMT acquired SL was treated by a Remex Luminescence Analyzer (Xi'an Remex Analyse Instrument Co., Ltd., China). UV/Vis absorption spectra were recorded by a TU-1091 UV/Vis spectrophotometer (Beijing PuXi Tongyong Analytical Instrument Co., Ltd., China). SL spectrum was recorded by a 970 CRT spectrofluorimeter (Shanghai Analytical Instrument Co., Ltd., China). Gold nanoparticles were characterized by a JEM-2100 Transmission Electron Microscope (TEM, JEOL, Japan) with an accelerating

voltage of 200 KV. A LC-20AT high performance liquid chromatograph (Shimzdzu, Japan) equipped with a SPD-20A UV/Vis detector, an Inertsil ODS-SP C_{18} column (4.6 mm × 250 mm) and LC-solution data acquisition software, was used to perform the official method for milk products. A 90:10 (v/v) mix of ion-pair reagent-buffer (sodium octanesulfonate, citric acid, pH=3) and acetonitrile was used as the mobile phase at a constant flow rate of 0.5 mL/min with an injection volume of 20 μL and column temperature at 40 ℃.

Sample preparation

Sample treatment was performed according to the literature with slight modifications.[35] A certain amount of milk sample (liquid milk or water dissolved milk powder) was transferred into a 25 mL nessler tube. 1.0 mL of 0.10 M ammonia and 2.0 mL of methanol were added to the sample, respectively. Then, this solution was shaken in order to promote the protein precipitation. Kept still for 5 min, 10 mL ethyl acetate was added into above mixture to extract melamine with the aid of ultrasound irradiation for 4 min. After centrifuged at 10000 rpm for 5 min, 6.0 mL of ethyl acetate phase was transferred into a 10 mL beaker. Evaporated at 60 ℃, ethyl acetate was completely removed in argon atmosphere. The finally obtained residue was dissolved in 5 mL water and further diluted to appropriate concentration before sampling.

Procedures

0.9 mL melamine standard/sample solution was mixed with 1.5 mL AuNPs solution for 7 min at room temperature. Subsequently, 6 mL deionized water was added into the above mixture to prepare the test solution. This test solution was centrifuged at 4000 r min^{-1} for 3 min. Then, 6 mL of supernatant was injected into the SL vial as the detection solution. The time controller was turned on with the preset cyc-working programme of 0.1 s on and 8 s off. SL intensity was recorded as a function of time by a data acquisition interface equipped with Remex Luminescence Analyzer. After each detection, the waste detection solution was removed and the SL vial was washed with 10 mL deionized water for three times. Melamine concentration was calculated by quantifying the net SL signal (ΔI), ΔI = I-I$_0$, where I and I$_0$ are the SL peak intensities corresponding to standard/sample and blank, respectively.

Results and discussion

Principle of SL method

The working principle of this AuNPs-SL design is summarized in Fig. 1. SL spectrum of air saturated water (0.21 mM sodium citrate) has been demonstrated to provide light emission over the 200-800 nm range. With the use of an interference filter as the monochromator, SL in band pass of 520±15 nm can be used as an endogenous light source whose intensity variation can be sensitively detected with the PMT. The synthesized 13 nm AuNPs possesses strong light absorption peaking at 520 nm. As anticipated, greatly quenched SL is found when detecting a blank AuNPs solution. As showed in the TEM and UV/Vis results (Fig. 1C), melamine causes obvious aggregation of AuNPs and shifts the peak absorbance from 520 nm to 715 nm. As a result, the quenched SL at 520 nm is greatly restored. Above results indicate

that the aggregation extent of AuNPs can be characterized by measuring the restored 520 nm SL. Consequently, any molecule that can interact with AuNPs to form the aggregates can be detected.

Method establishment

To establish our AuNPs-SL method, all device parameters and experimental variables including the ultrasound irradiation duration, the interval between two irradiations, composition of test solution, and interaction time of AuNPs and melamine, were investigated with the aim to achieve the best sensitivity and acceptable reproducibility. For each detection solution, seven replicate measurements were performed unless otherwise; the detection reproducibility was evaluated by the relative standard deviation (RSD).
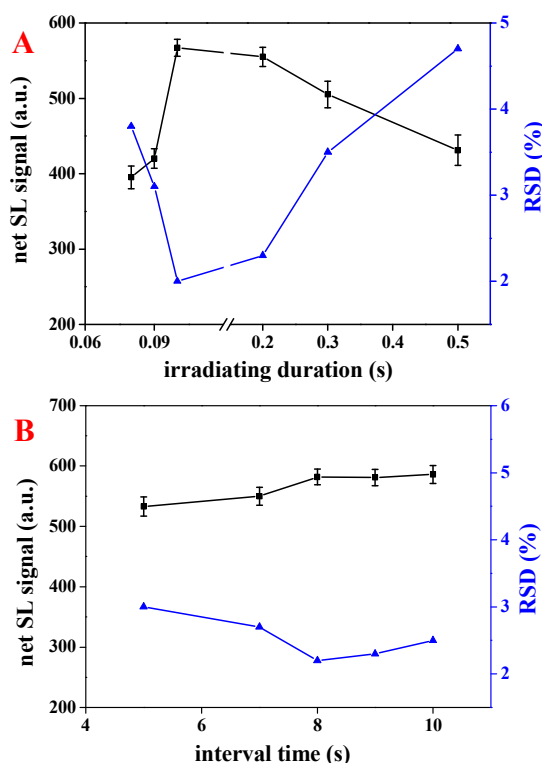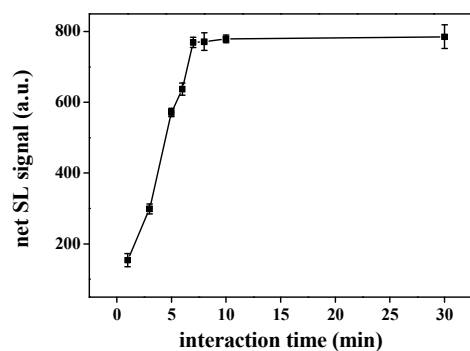
Fig. 2 Effects of (A) ultrasound irradiation duration and (B) interval on SL detection of 1.0 μM melamine. AuNPs and melamine interaction time, 5 min; volume of detection solution, 6 mL; PMT, biased at -700V. Error bar represents the standard deviation for seven measurements.

The firstly investigated parameter is the ultrasound irradiation power applied to detection solution. The water SL was found increasing with the raise of ultrasound power. To approach the strong SL, the humidifier power output was set at its maximum with the estimated ultrasound power of 2 W/cm^2. The ultrasound irradiation duration is known a key parameter that affects the SL intensity and reprocucibility.[32] The temperature of detection solution increases as a consequence of the high temperatures generated within collapsing microbubbles. Thus, short irradiation duration is relatively preferable to maintain the temperature of detection solution so as to achieve the reproducible SL signals. In this work, the effect of irradiation duration on net SL signal was

investigated by varying this duration from 80 ms to 500 ms. Observing the experiment results showed in Fig. 2A, it is found that when the duration is set at 100 ms, the strongest SL signal is obtained for 1.0 μM melamine standard with the RSD less than 5%. An irradiation interval is set for the cooling down of detection solution. This interval affects both the signal reproducibility and the detection frequency. By varying the interval from 4 s to 10 s, we find that when it is 8 s or longer, the net SL signals are getting stable with all the RSDs inferior to 5% (Fig. 2B). In the following experiments, the 8 s interval is selected as the optimum. This interval plus previous irradiation duration theoretically conspires to allow a detection frequency of 7.4 times min^{-1}.

The content of AuNPs in test solution plays an important role in method sensitivity. In principle, our SL detection is based on both the water SL quenching by dispersing AuNPs and the SL restoring by melamine resultant AuNPs aggregation. On one hand, the high AuNPs concentration facilitates the efficient SL quenching and the weak SL background; On the other hand, the low AuNPs concentration facilitates the sensitive aggregation and SL response to melamine. Experiments to investigate the effect of AuNPs content on sensitivity were performed with a 1.0 μM melamine standard as showed in Fig. S2. The best SL response is found by utilizing 1.5 mL AuNPs to compose the test solution. For such AuNPs content, the sodium citrate concentration is estimated to be 0.21 mM and the acidity of test solution is pH 6.40. The mixing order of AuNPs, melamine, and water was found affecting the SL detection sensitivity. Experiments show that when standard/sample was arranged to mix and interact with AuNPs prior to water dilution, the best SL response is obtained (Fig. S3).

Fig. 3 Effect of interaction time between melamine and AuNPs on SL detection. Melamine, 1.0 μM; ultrasound irradiation duration, 0.1 s; ultrasound irradiation interval, 8 s; test solution composition, 1.5 mL AuNPs; test solution in vial, 6 mL; PMT, biased at -700V. Error bar represents the standard deviation for seven detections.

To fit the size of the available ceramic transducer, a 15 mL glass vial was used to construct the SL vial. Such a vial requires the mL level of detection solution to complete the SL measurement. This leads to our consideration on the cost of AuNPs. To alleviate the AuNPs consumption, as detailed in procedures section, we diluted the 2.4 mL mixture of AuNPs and melamine with water to 8.4 mL. Relative experiments indicate that the volume of detection solution (in SL vial) also affects the detection sensitivity. On one hand, the large volume of detection solution

provides the large detection zone and the strong SL. On the other hand, the large volume of detection solution leads to the decrease of ultrasound power density, as well as the decrease of SL. By varying this volume from 3.0 mL to 8.0 mL, as showed in Fig. S4, 6.0 mL of detection solution is finally selected as the optimum.
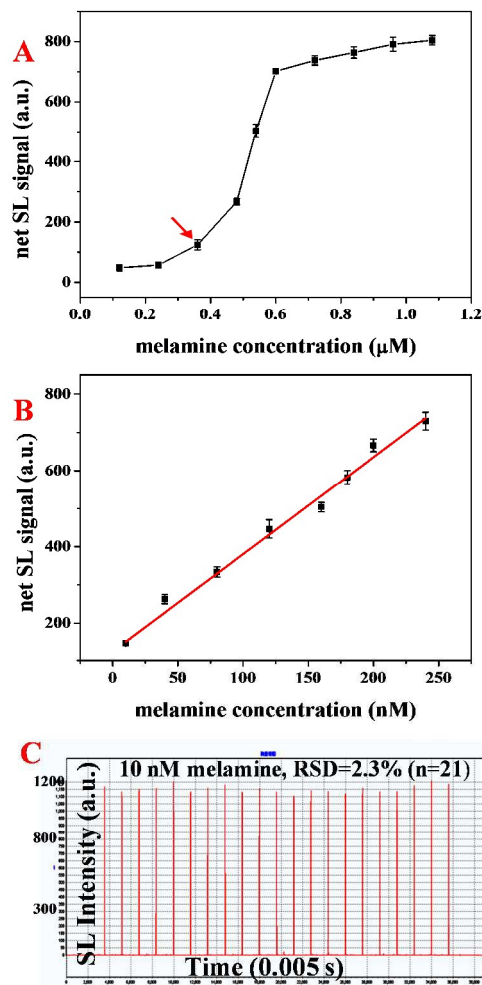
Fig. 4 (A), The corresponding plot of net SL signal versus melamine concentration. (B), Calibration curve of melamine. (C), A chart recording of the detection reproducibility experiment results for a 10 nM melamine standard. Red arrow represents the commencement of "jump range"; error bar represents the standard deviation for triplicate measurements.

An interaction time of 5 min is previously thought sufficient to complete the interaction between melamine and AuNPs when observing the UV/Vis absorption at 520 nm. Nevertheless, more experiments found the different story for our SL detection. The effect of interaction time on SL detection was examined by varying the time from 1 min to 30 min. As showed in Fig. 3, the SL signal increases gradually over time, and reaches a plateau after 7 min. We supposed that it takes time for melamine to form the steady AuNPs aggregates in micro to resist the ultrasonic dispersing. To boost detection frequency, 7 min was selected as the optimal interaction time. Dispersing nanoparticles with ultrasound irradiation to prevent their self-aggregation is a

commonly adopted technique in nano-material preparation and utilization. Considering the 2 W/cm^2 ultrasound power applied to 6 mL detection solution, the transient sound power density is generally much bigger than that for nanoparticles dispersion. So, the self-aggregation of AuNPs can be neglected by SL detection.

This also implies that SL detection is potentially able to distinguish the strong molecule-AuNPs interaction (e.g. melamine sourced aggregation) from the weak ones. This potential is expected to be an advantage for selective detection.

Table 1 Comparison of analytical performance with nano-materials based methods

Methods	Linear range (µM)	Detection limit (µM)	Ref.
Visualization, AgNPs	-	0.0793	18
Electrochemical, ordered mesoporous carbon	0.05-7.0	0.24	19
Resonances cattering, aptamer-modified AgNPs	0.158-0.84	0.0792	20
SPR, polythymine-stabilized AuNPs	0.08-1.0	0.02	21
Dynamic light scattering, AuNPs	0.396-9.91	0.396	25
Surface enhanced Raman spectroscopy, AuNPs	2.45-39.6	1.348	26
Fluorescence energy transfer, CdTe/CdS QDs and AuNPs	0.05-1.0	0.05	29
Fluorescence energy transfer, fluorescence probe and AuNPs	0.01-4.0	0.003	30
Visualization, AuNPs	-	0.1982	38
Fluorescence energy transfer, rhodamine B and AuNPs	0.0396-7.93	0.0014	39
Colorimetry, AuNPs	0.39-3.97	5.56	40
Fluorescence energy transfer, carbon dot and AuNPs	0.05-5.0	0.036	41
Sonoluminescence, AuNPs	0.01-0.24	0.003	our

Analytical performance

After the establishment of the SL system as described above, its analytical capabilities were investigated. By varying melamine concentration in the range of 0.12 µM to 1.08 µM, a titration curve like relationship between the net SL signals and melamine concentrations is found in Fig. 4. As can be seen, the melamine responsive SL signals vary slightly when the melamine concentrations are lower than 0.36 µM or are higher than 0.60 µM in difference with jump SL responses to melamine ranged from 0.36 to 0.60 µM. This phenomenon is attributed to the unique nonlinear optical properties of AuNPs as discovered in reported researches.[22,36-38] According to the molecular-linker-based aggregation mechanism,[38] free melamine at about 1.0 µM level would not lead to the significant AuNPs aggregation for the immediate exhaustion of melamine, the strong adsorption at the surface of AuNPs. With the melamine concentration increase, initial crosslinkage among AuNPs takes placed through the multiple binding sites of melamine molecule. Then after, trace excessive melamine causes further crosslinkage among the small AuNPs aggregates to form the big 3D aggregate. At this stage, melamine concentration variation at nM level gives rise to the obvious color change, as well as the obvious SL response in this work. Finally, the further supplied free melamine would not cause the further aggregation, the SL increase calms down. To achieve the sensitive melamine detection as well as the wide calibration range, according to the reported strategy,[22,37] 0.36 µM melamine standard was added into the test solution in advance to prepare the "jump range" background. As showed in Fig. 4B, experiments find the linear relationship between net SL signals and melamine concentrations from 10 nM to 240 nM following the equation of $\Delta I = 25.5\ C\ (10\ nM) + 125.9$ with a correlation coefficient of 0.991 (n=9). According to the 3σ rule, the limit of detection was calculated to be 3 nM melamine. According to literature,[39] the absorption of melamine may neutralize the surface charge of AuNPs and lead to dispersion of AuNPs in the NP cluster due to electrostatic repulsion. Fig. 3 demonstrates that the melamine cross-linked AuNP aggregates can keep stable for at least 30 min. To promise the reproducible SL, AuNP aggregates were removed via centrifugation. By replicating detection of a 10 nM melamine standard for 21 times, the SL method reproducibility was investigated. Experiment result showed in print screen copy in Fig. 4C indicates the acceptable reproducibility. Such reproducibility is also attributed to that the SL signal is collected as the integration over the 520±15 nm wavelength range rather than at 520 nm only. In addition, since the absence of external light source for SL detection, the relative dark background benefits to achieve the high sensitivity. A comparison on analytical performance of SL method with literature methods is listed in Table 1. Even the presented home-use humidifier SL system cannot promise the best sensitivity since the known dependence of water SL on acoustic frequency,[40] our work takes advantage in sensitivity over most of that reported. Along with the significance in low-cost and easy instrument availability, the robust of SL technique has been showed enough.

Table 2 Interference experiment results

Substance	Tolerable concentration ratio
Ca^{2+}, Zn^{2+}, NO$_3^-$, PO$_4^{3-}$, Phenylalanine	500
Na$^+$, Fe^{3+}, Mg^{2+}, K$^+$, SO$_4^{2-}$, Glucose, Lactose Lysine	100

In order to evaluate the selectivity of SL detection toward melamine, some ions and small molecules that possibly coexist in milk products were investigated by analyzing a melamine standard to which increasing amount of interfering substances were added. The tolerable concentration ratios with respect to 100 nM standard for interference at less than 5% level are listed in Table 2. The proved selectivity toward melamine matches with or surpasses those in reported AuNPs-based methods.[21,23,41-43] As discussed in previous section, the SL detection is able to distinguish the steady AuNPs aggregates from the weak ones. Trace amount of volatile compound is known influencing water SL.[44] To prevent the possible interference from volatile organic compound, ethyl acetate for melamine extraction from milk samples was completely removed as described in sample preparation section. Based on above proved selectivity, our SL method is supposed to differentiate melamine from other common ions and small molecules in real samples.

Application to milk samples

To evaluate the feasibility of proposed AuNPs-SL method, we applied it to detection of melamine in three real samples, including two of liquid milk products and one milk powder product. These samples were found melamine free by both our SL method and official method (GB/T 22388-2008). As a result, spiking samples were prepared by randomly doping melamine into the three milk products. Their melamine contents were analyzed according to the described procedures for sample

preparation and melamine detection. As showed in Table 3, our SL results are in agreement with those obtained through official method. Statistical analysis results indicate that there are no significant differences in precision and accuracy between SL method and official method at 95% confidence level using tabulate F value of 19.00 and t value of 2.78. All these results signify the capability of our method for the sensitive detection of melamine in milk products.

Table 3 Results of melamine analysis for milk samples

Samples	This method (mg kg^{-1} ±SD)^a	Official method (mg kg^{-1} ±SD)^a	Difference (%)	F value	t value
				α=0.05	
liquid milk 1	1.10 ±0.06	1.14±0.04	-3.5	2.25	0.97
liquid milk 2	53.31 ±1.51	53.48±2.51	-0.32	2.78	0.10
milk powder	27.40 ±0.19	27.17±0.23	+0.85	1.47	1.33

^{a} Triplicate measurements.

Conclusion

With all the experiment results obtained in this work, the described AuNPs-SL design proposes a promising new way for melamine analysis. By converting the melamine responsive aggregation of AuNPs into SL signal, melamine can be sensitively quantified. The studied method has been successfully used for the detection of melamine contents in real milk products with official method validation. This work provides some potential interests, (1) light emission detection without the requirement of external light source or luminescent reagents; (2) integration of nano-material and SL; (3) inexpensive equipment, easy operation, and high throughput detection. It is expected that our design can be an example to arouse the interest of analysts to utilize SL as an alternative tool for new nano-materials based SL techniques.

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Notes and references

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