We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter 8

Surface-Enhanced Raman Scattering Liquid Sensor for Quantitative Detection of Trace Melamine in Dairy Products

Mingqiang Zou, Xiaofang Zhang, Xiaohua Qi and Feng Liu

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/52485

1. Introduction

Raman spectroscopy has emerged as a fast, non-invasive, analytical method for the detection and quantification of adulterants in many fields (Wong et al., 2007; Weng et al., 2003; Muik et al., 2003; Micklander et al., 2002; Peica et al., 2005; Rubayiza et al., 2005; Ellis et al., 2005; Paradkar et al., 2001; Abalde-Cela et al., 2009; Mulvihill et al., 2008; Zhou et al., 2006). Although signals from conventional Raman spectroscopy are very weak, great progress has been made with the development of surface-enhanced Raman spectroscopy (SERS) as a sensing method. SERS is a powerful spectroscopy technique that can provide ultra-sensitive characterization of adsorbate molecules on roughened metal (e.g., Ag, Au, and Cu) surfaces that produce a large enhancement to the Raman scattering signal (Lin et al., 2008; Lee et al., 1982; Wei et al., 2009; Küstner et al., 2009; Koglin et al., 1996; House et al., 2008; Leopold et al., 2003; Yaffe et al., 2008; Yu et al., 2007; Tiwari et al., 2007; Guingab et al., 2007; Tian et al., 2002; Wang et al., 2005; Chen et al., 2012; Betz et al., 2012). Generally, solid/liquid substrates are necessary to enhance the SERS spectrum to obtain adequate sensitivity.Solid substrates, generally prepared as gold or silver nanoparticles with a silica or alumina shell, have a wide application range. However, only a few examples of liquid substrates have been reported, though they are easily prepared and enhance the analysis some analytes.For example, using a silver colloid, at least a 10^5-fold enhancement of the Raman signal is achieved for the measurement of melamine (Zou et al., 2010).

Presently, there are two commonly accepted sensing mechanisms(Chu et al., Phys. Rev; Campion et al., 1998; Knoll, 1998; Kneipp et al., 1999; Moskovits et al., 1998; Otto et al. 2005):

INTECH
open science | open minds

© 2013 Zou et al.; licensee InTech. This is an open access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

the electro-magnetic enhancement mechanism, which involves enhancement in the field intensity by plasmon resonance excitation; and the chemical enhancement mechanism, which involves enhancement of the polarizability by chemical effects such as a charge-transfer excited states.The efficiency of the generation of the SERS signal is high enough to observe the Raman spectrum of even a single molecule. With the rapid development of nanofabrication technology, SERS has grown to become a very active field of research in several areas of materials and analytical sciences, such as medicine, the environment, food, gems, cultural relics, and archaeology (Fan et al., 2011; Jun et al., 2010; Deiss et al., 2011).

In the following section, liquid milk melamine detection using a SERS liquid sensor is described as an example of this technique. In the example, liquid milk samples preparation process is very easy, i.e. only diluted with double-distilled water and centrifugation is required. With the aid of silver colloid, at least a 10^5-fold enhancement of the Raman signal was achieved for the measurement of melamine. The limit of detection by this method was 0.01 g mL^{-1} for melamine standard samples. Based on the intensity of the Raman spectroscopy with vibration bands normalized by the band at 928 cm^{-1} (CH2), external standard method was employed for the quantitative analysis. The linear regression square (R^2) of curve was 0.9998, the limit of quantitation using this approach was 0.5 g mL^{-1} of melamine in liquid milk, the relative standard deviation was ≤ 10% and recoveries were from 93 to 109%. The test results for SERS were very precise and as good as those obtained by LC/MS/MS.

2. Background of surface-enhanced Raman scattering liquid sensor for melamine detection

Since 2008, there has been mounting concern about the intentional adulteration of protein ingredients in milk powder with melamine, because milk powder blended with melamine can lead to kidney disease and even death in babies. Thisfear of milk powder tainted with melamine has an important influence on the dairy production of milk powder and cow breeding, as well as an important impact on the food market and industry. Currently, new methods such as high-performance liquid chromatography (HPLC) (Ehling et al., 2007; Muniz-Valencia et al., 2008), liquid chromatography coupled with mass spectroscopy (LC-MS) (Varelis et al., 2008), LC-MS/MS (http://www.cfsan.fda.gov/~frf/lib4421.htm), thin-layer chromatography (TLC) (Broszat et al., 2008), commercial enzyme-linked immunosorbent assay technology (Eric et al., 2008), matrix-assisted laser desorption/ionization mass spectrometry (Tang et al., 2009), and surface desorption atmospheric pressure chemical ionization mass spectrometry (Yang et al.,2009) are the principal analysis techniques used for the detection and quantification of melamine in food. However, these methods are time consuming and cannot satisfy the need for melamine detection in practice because raw milk spoils and must be assayed within 4 h. Moreover, these methods require access to complicated and expensive laboratory facilities, especially in terms of sample preparation and clean-up steps. Therefore, it is of particular importance to develop a simple, quick, cost-effective, and sensitive method for detection of melamine in food.

http://dx.doi.org/10.5772/52485

We demonstrate an approach to detect melamine in liquid milk using surface-enhanced Raman spectroscopy in a silver colloid, which can be used for the rapid and online detection of melamine in dairy products.

2.1. Optimization of the surface-enhanced Raman scattering liquid sensorfor melamine detection

In recent years, gold nanoparticles (Au NPs) and silver nanoparticles (Ag NPs) have been widely used as colorimetric probes for chemical sensing and biosensing of various substances (Zhao, et al., 2008), such as viruses (Niikura et al., 2009), protein (Wang et al., 2008), DNA (Cho, et al., 2008), cancerous cells (Medley et al., 2008), and small molecules (Chen, et al., 2010; Li et al., 2009; Zhang et al., 2008), relying on their unique size-dependent and/or interparticle distance-dependent absorption spectra and solution color. For example, triple hydrogenbonding recognition between melamine and a cyanuric acid derivative grafted on the surfaced of Au NPs can be used for reliable detection of melamine (Ai et al., 2009).

Currently, much attention has been paid to the study of the optical absorption spectra of nanoscale colloidal silver in the quest for SERS enhancement factors. Compared to Au NPs, Ag NPs have some advantages, for example, lower cost of preparation and higher extinction coefficients relative to Au NPs of the same size (Lee, et al, 2007). Therefore, Ag NPs are also good candidates for melamine sensing (Han, et al., 2010; Ping et al., 2012).

Upon considering the influence of temperature, ionic strength, and aggregation behavior of colloids on the SERS spectra band intensity in the presence of adsorbates and the wavelength at which maximum enhancement occurs, the latter shift to higher values with time. In particular, the adsorption of the colloid is strongly influenced by chloride ions (Koglin et al., 1996) and pH (House et al., 2008). Scanning electron microscopy images of a silver colloid before and after addition of reagent A (Sodium chloride aqueous solution or aqueous potassium chloride solutions) and reagent B (Aqueous sodium hydroxide or potassium hydroxide solution) are presented in Figure 1. As shown in Figure 1a, the colloidal silver particles mainly displayed a spherical morphology with a uniform size of ~70-100 nm. After added reagent A (Fig. 1b) or reagent B (Fig. 1c), the silver colloid became aggregated and inhomogeneous. When reagents A and B were added to the colloidal silver at the same time, the morphology of the silver colloid became more dense and uniform (Fig. 1d), which is the best form for SERS enhancement. Thus, this system was chosen as the surfaced-enhancing substrate for further study. Figure 1e shows the SERS spectra of 1 μg mL^{-1} melamine on the corresponding enhancing substrates from (a), (b), (c) and (d) in Figure 1. There are no evident Raman bands of melamine on silver colloid (curve ◎in Fig. 1e) or on silver colloid with reagent A (curve ◎in Fig. 1e). However, when reagent B was added to the silver colloid (curve◎in Fig. 1e), a weak characteristic peak of melamine was observed at 698 cm^{-1}, i.e., the SERS spectra band intensity was affected by pH. After reagents A and B were added to the silver colloid (Curve IV in Fig. 1e), the characteristic peak of melamine was strongly enhanced, with the intensity of the peak at 698 cm^{-1}being the greatest.

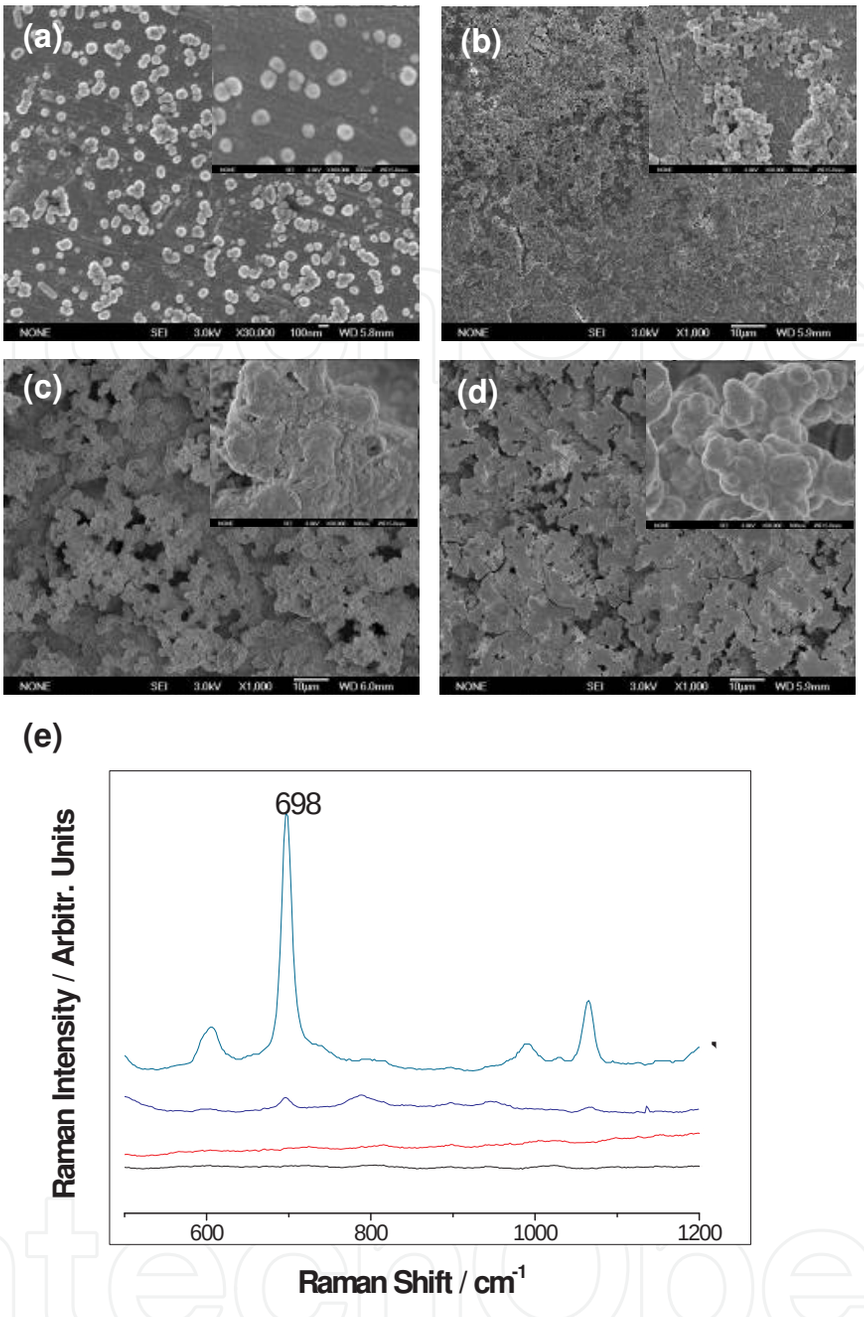

Figure 1. a-d) Scanning electron microscopy images of colloids and(e)SERS spectra of 1 μg mL^{-1} melamine with the corresponding enhancing substrates.Scanning electron microscopy images of silver colloids (a)before and(b) after addition of reagent A, (c) reagent B, and (d) reagents A and B together.(e) Curves ?,?,? and ?are SERS spectra of 1 μg mL^{-1} melamine from the corresponding enhancing substrates from (a), (b), (c), and (d), respectively.

2.2. Description of use of the milk melamine liquid sensor

It is believed that melamine (2,4,6-triamino-1,3,5-triazine) is sometimes intentionally added to food ingredients to make the products appear to contain higher protein levels due to the high nitrogen content of melamine. A safety limit for melamine ingestion is officially set at 2.5 ppm for adult food and 1 ppm infant formula by the US Food and Drug Administration (Zhao et al.,

http://dx.doi.org/10.5772/52485

2009; http://www.fda.gov/NewsEvents/ Newsroom-/ PressAnnouncements/ 2008/ ucm116960.htm.). The maximum residue level of melamine in infant formula is now legally regulated at 1 ppm by the Chinese government after the recent melamine accident (Guo et al., 2010). To achieve this lower limit of detection (LOD), silver colloids are ideal candidates to be used as surfaced-enhancing substrate liquid sensors due to their strong Raman-enhancing effect. Thus, we chose silver colloid as a surfaced-enhancing substrate for the detection of melamine in this study, and the detection process is diagrammed in Figure 2.First, liquid milk was diluted with double-distilled water (Fig. 2a) toobtain a diluted milk sample. Next, the diluted sample was placed into a 1.5-mL conical centrifuge tube and centrifuged for 4 min at 14,000 rpm, and then it was delaminated (Fig. 2b). Next, the supernatant was removed from the centrifuge tube and was added to the silver colloid, which was previously prepared with dropwise addition of reagents A andB, and uniformly mixed (Fig. 2c).Finally, the SERS spectra were recorded using a portable Raman spectrometer (Fig. 2d) to collect analytical results.

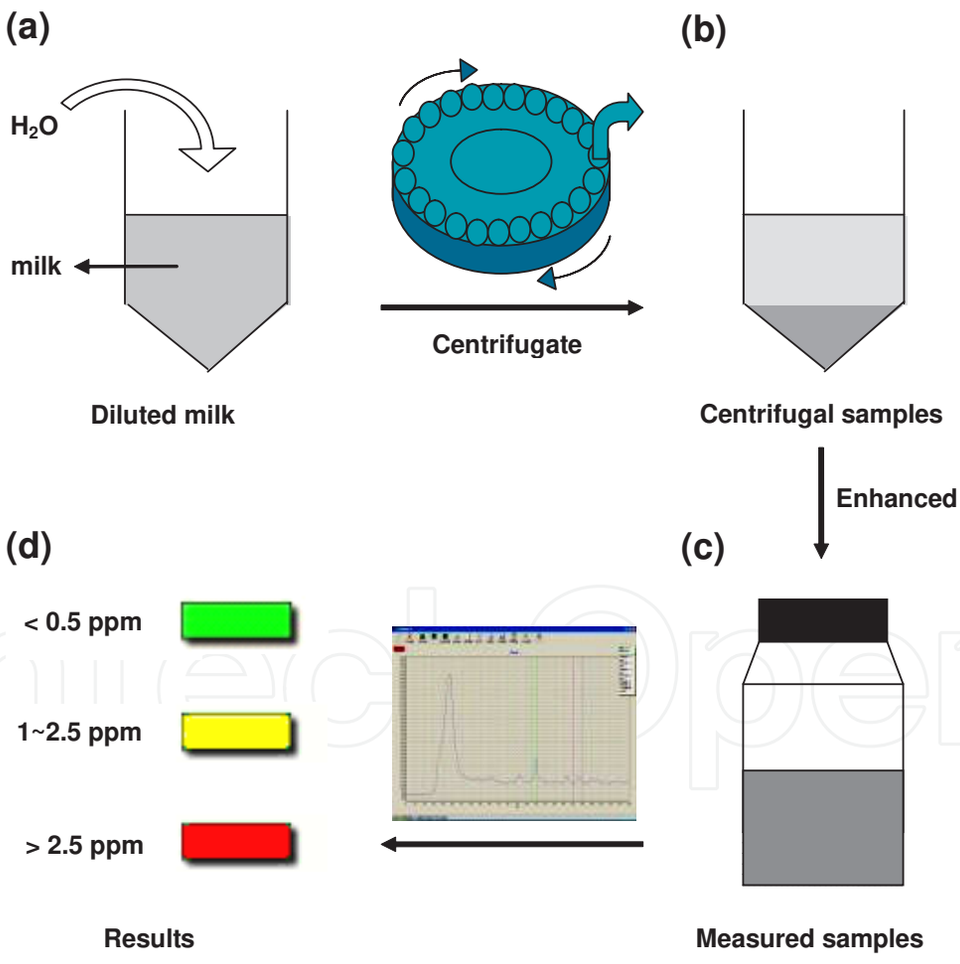

Figure 2. Schematic diagram of the on-line and rapid method for measuring melamine in liquid milk using surface-enhanced Raman spectroscopy.(a) Liquid milk was first diluted with double-distilled water.(b) The diluted sample was then centrifuged and delaminated.(c) The supernatant was addedto the silver colloid.(d) SERS spectra were recorded using a portable Raman spectrometer.

2.3. Optimization of the melamine spectra

Based on these experimental results, the spectra of different concentrations of melamine in solution were investigated from 500–1200 cm^{-1}, as shown in Figure 3.Typical Raman peaks of solid melamine at 382, 584, 678, and 983 cm^{-1} were observed (Fig. 3a).The most intense peak at 678 cm^{-1} is assigned to the ring breathing II mode, which involves in-plane deformation of the triazine ring. And the second most intense peak at 983 cm^{-1} arises from the ring breathing mode I of the triazine ring (Koglin et al., 1996). The peaks at 698 and 1005 cm^{-1}, visible in the SERS spectra of Figure 3b–d, were obtained from melamine samples at concentrations of 5×10^{-1}, 10^{-1}, and 10^{-2} μg mL^{-1}. The Raman spectra of the enhanced substrate, i.e., silver colloid treated with reagents A and B,is shown in Figure 3e.In the absence of melamine, small peaks at 698 and 1005 cm^{-1} were observed, and the other peaks disappeared. Only a small peak at 678 cm^{-1} was observed in the Raman spectra of melamine dissolved in water (Fig. 3f), and no peaks were evident in the spectra obtained from the 10^{3} μg mL^{-1} melamine sample in the absence of the enhancing substrate (Fig. 3g).

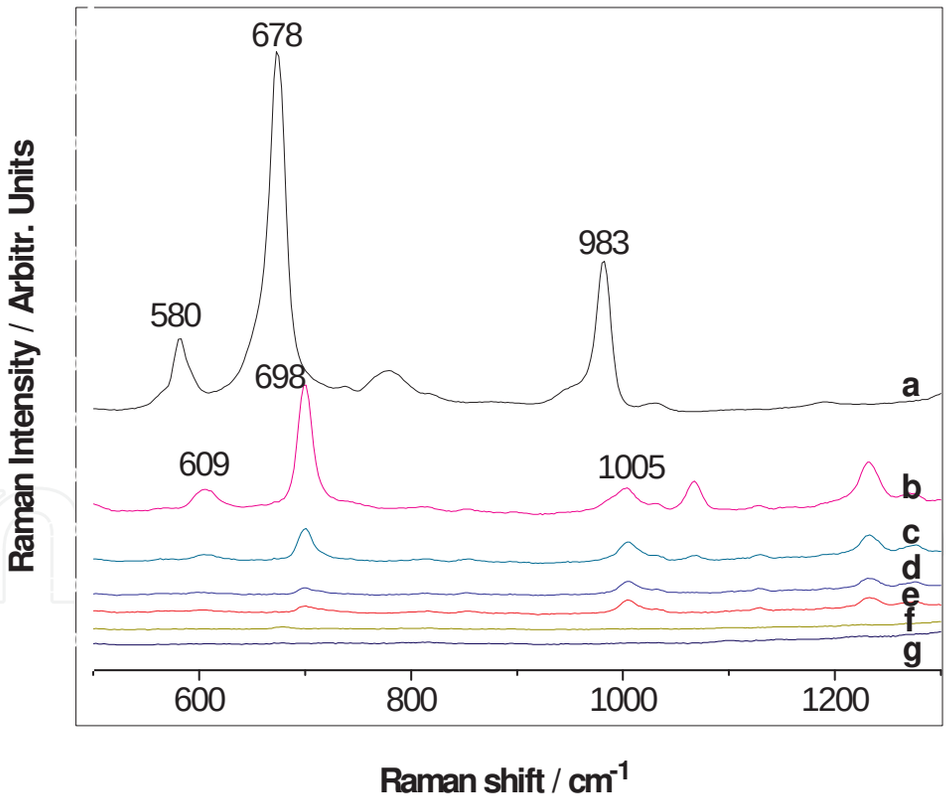

Figure 3. Raman spectra and SERS spectra of melamine at different concentrations.(a) Raman spectra of solid melamine.SERS spectra of melamine solution at (b) 5×10^{-1} μg mL^{-1}, (c) 1×10^{-1} μg mL^{-1}, and (d) 1×10^{-2} μg mL^{-1}.Raman spectra of silver colloid treated with reagents A and B (e) and melamine at different concentrations: (f) ~3.3×10^{3} μg mL^{-1}; and (g) 1×10^{3} μg mL^{-1}.

http://dx.doi.org/10.5772/52485

2.4. Analysis of detection results

To demonstrate the practical application of melamine in liquid milk, we used melamine in raw liquid milk as an example. Various concentrations of melamine in liquid milk were extracted and analyzed by their SERS spectra (Fig. 4). As shown in Figure 4a, seven concentrations (0.5, 1, 2, 2.5, 5, 8, and 10 μg mL^{-1}) of melamine in liquid milk were studied, and the intensity of the melamine peak at 698 cm^{-1} was enhanced with increasing melamine concentration. To eliminate the effects of the matrix and other factors (e.g., temperature, humidity, and focal distance), the intensity of the peak at 928 cm^{-1} was set at 100 for milk, and the Raman peak at 698 cm^{-1} in the absence of melamine had a fixed value. Accordingly, a melamine standard curve was obtained by establishing a plot correlating the melamine concentrations in liquid milk to the intensity of the intense SERS spectral peak of melamine at ~698 cm^{-1}. A linear regression (R^2 = 0.9996) was found between the Raman intensity and melamine concentration (Fig. 4b). The limit of quantification (LOQ) using this approach to detect melamine in liquid milk was also investigated, as shown in Figure 5. We found that this specific approach is reasonable for the detection of melamine in liquid milk because only one prominent peak was present in the melamine SERS spectra, which can be applied to field detection of various liquid milk products.

Moreover, the tests were performed and assessed by the Ministry of Science and Technology of the P. R. China, complying with the general administration quality supervision inspection quarantine of the P. R. China, the Ministry of Agriculture of the P. R. China, the Ministry of Health of the P. R. China, and the National Institute of Metrology P. R. China. The SERS test results were very precise and as good as those obtained by the LC/MS/MS method (Table 1). Forty-nine of 50 test samples results were correct, i.e., melamine was correctly detected in 98% of the test samples (Table 2).The concentration error in the samples was 0.2 ppm, which exceeds the limit of quantification using Raman spectra. The relative standard deviations (RSDs) were ≤ 10%, and the relative measurement deviations (RMD) were ≤ 10%.Therefore, the SERS method is an effective approach for measuring liquid milk melamine, which provides on-line, rapid, and reliable screening.

Sample #	LC/MS/MS (μg mL^{-1})	Quantity	Quality
No.1	2.37	2.6	Positive
No.2	2.37	2.5	Negative
No.3	0.48	1.1	Negative
No.4	7.20	7.5	Positive
No.5	2.37	2.8	Positive
No.6	2.37	2.7	Positive
No.7	≤0.1	0	Negative
No.8	2.37	2.6	Positive
No.9	1.91	2.05	Positive

Table 1. Comparison of results obtained by Raman spectroscopy and LC/MS/MS of liquid milk from the first test.

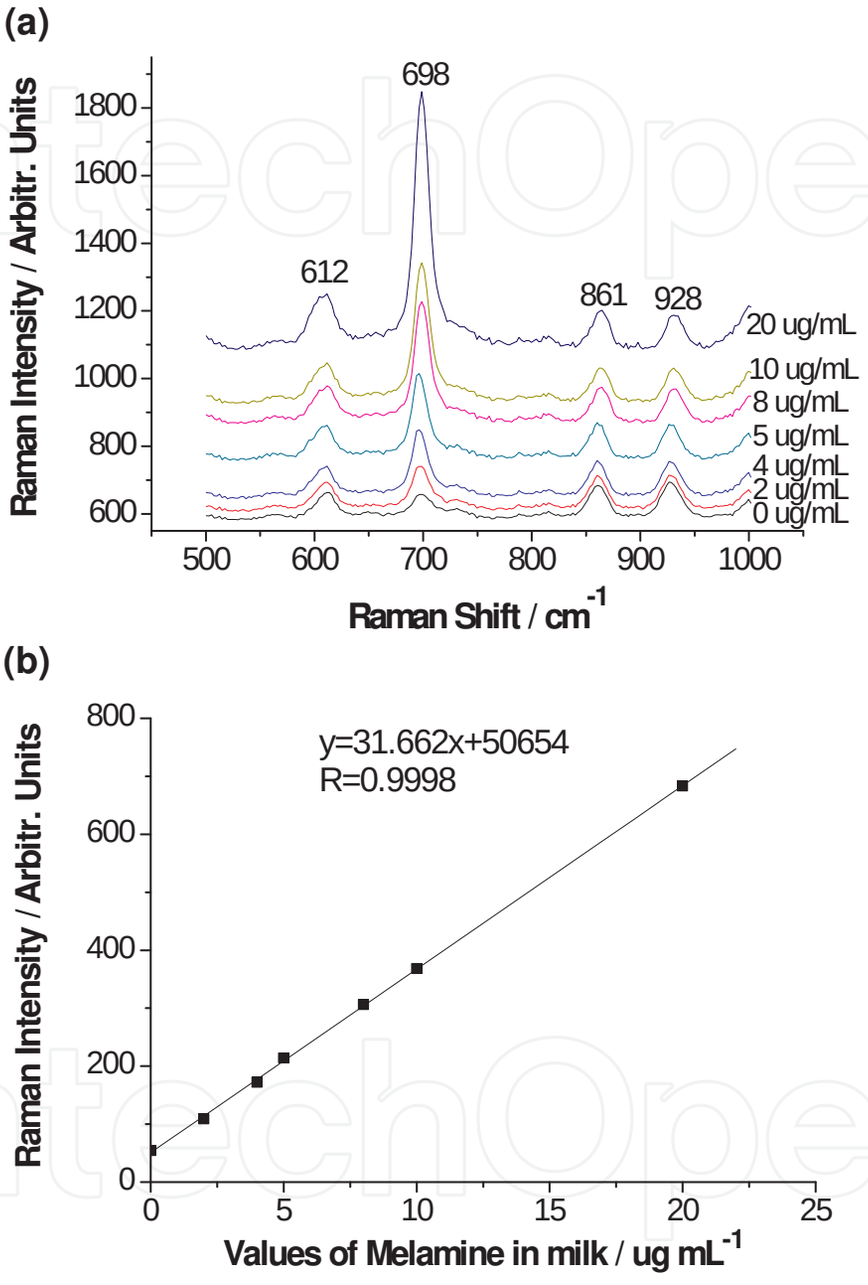

Figure 4. SERS spectra and standard curve of melamine in milk.(a) SERS spectra of different concentrations of melamine in milk. (b) Standard curve of melamine in milk.

http://dx.doi.org/10.5772/52485

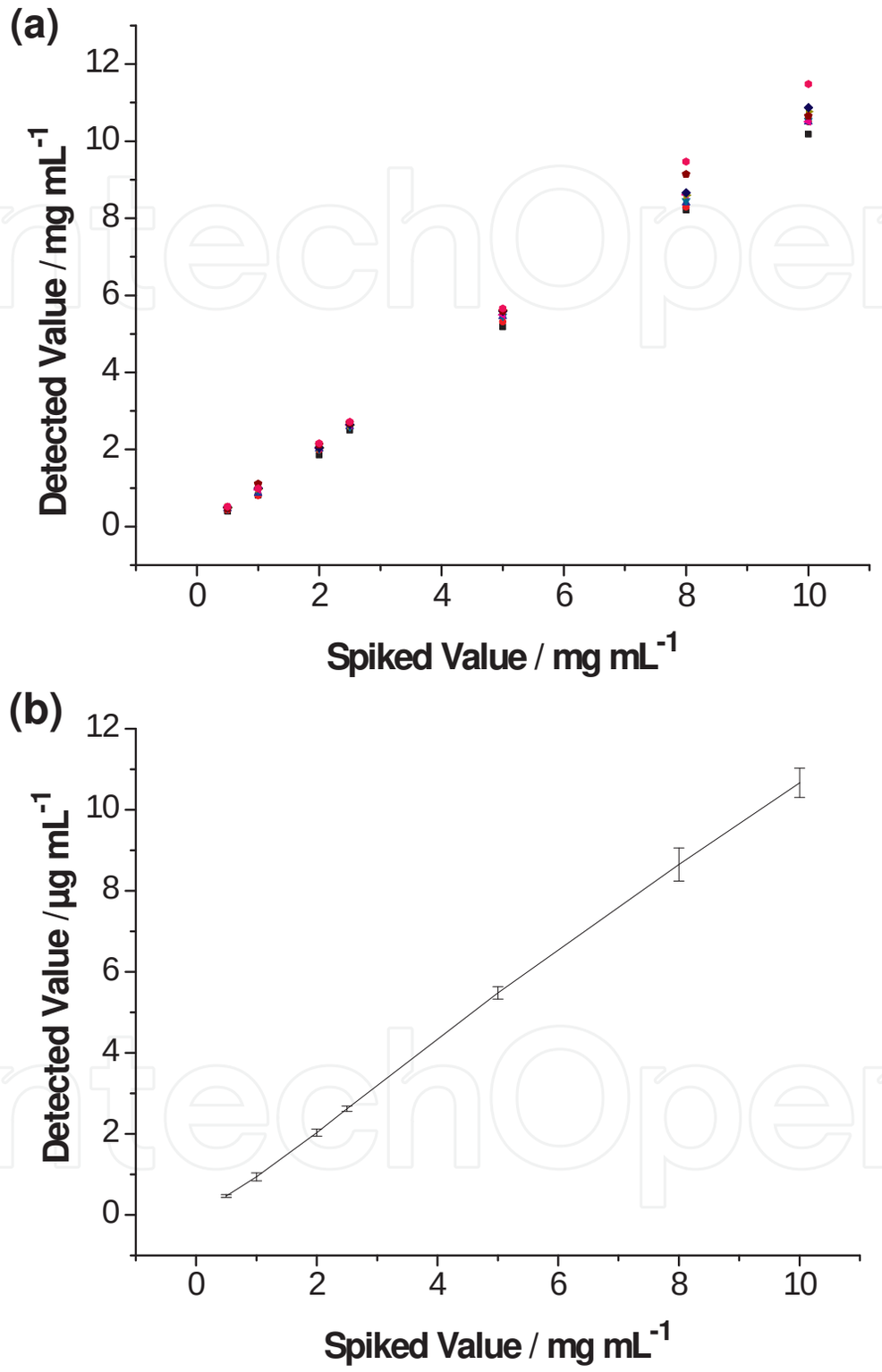

Figure 5. Predicted melamine value (µg mL^{-1}) compared to a spiked melamine value (µg mL^{-1}) using (a) the external standard method and (b) the error line. The spectral region = 1000-1800 cm^{-1}; spectral number n = 63.

Serial number	Random number	Raman (ppm)	LC/MS (μg mL^{-1})	Average value (μg mL^{-1})	RSD (%)	RMD (%)
1	754	0	<0.03			
2	769	0				
3	775	0				
4	781	<0.2				
5	788	0				
6	800	0				
7	695	0.19	0.20	0.25		
8	709	0.29				
9	719	0.24				
10	725	0.16				
11	731	0.28				
12	736	0.51				
13	741	0				
14	751	0.29				
15	658	0.57	0.50	0.55	10	0.10
16	669	0.52				
17	676	0.47				
18	684	0.58				
19	692	0.62				
20	700	0.54				
21	711	0.54				
22	606	1.19	1.02	1.07	10	0.10
23	617	1.08				
24	685	0.98				
25	694	1.01				
26	703	1.06				
27	708	1				
28	721	1.15				
29	451	2.26	2.02	2.23	2	0.10
30	523	2.14				
31	574	2.2				
32	611	2.23				
33	615	2.25				
34	620	2.3				
35	626	2.2				
36	634	2.23				
37	642	2.2				
38	652	2.22				
39	686	2.27				
40	589	28.37	30.25	30.78	6	0.02
41	590	32.69				
42	609	32.31				

http://dx.doi.org/10.5772/52485

Serial number	Random number	Raman (ppm)	LC/MS (μg mL^{-1})	Average value (μg mL^{-1})	RSD (%)	RMD (%)
43	621	33.4				
44	625	30.86				
45	644	29.97				
46	646	30.51				
47	691	28.1				
48	457	10.55	10.07	10.67	3	0.07
49	614	10.8				
50	683	11.15				

Table 2. Comparison of results obtained by Raman spectroscopy and LC/MS/MS of liquid milk from the second test.

A method was established to detect melamine in liquid milk using surface-enhanced Raman spectroscopy with the aid of a silver colloid enhancing substrate. An enhancement factor of ≥ 10^5-fold was achieved in the measurement of melamine on this SERS-active substrate. In addition, the milk sample preparation process used in this technique is easy and time-saving, only requiring four steps: dilution, centrifugation, addition of samples to the enhanced base, and collection of the Raman spectra. The total detection time using SERS to measure a sample was ~3 min, which is starting from the dilution up to the final results. And the Raman spectra were acquired for only 3 s. Based on the calculations of the most intense peak in the melamine SERS spectra at approximately698 cm^{-1}, the LOQ of the SERS spectra achieved a level of 0.01 μg mL^{-1} for melamine standard samples, which corresponds to 0.5 μg mL^{-1} melamine in liquid milk. The RSD was ≤ 10 %, and recoveries were from 93-109%.The results from actual sample analyses were very precise and as good as those results obtained by LC/MS/MS.

3. Summary

Melamine, a nitrogen-rich chemical, has recently caused enormous economic losses to the food industry due to instances of milk products being adulterated by melamine, which has led to an urgent need for a rapid and reliable detection method for melamine in food. Here, we used a SERS liquid sensor to detect melamine in dairy products. The preparation processfor the dairy product samples is very easy, i.e.,only dilution with double-distilled water and centrifugation is required.With the aid of a silver colloid, at least a 10^5-fold enhancement of the Raman signal was achieved for the measurement of melamine. The LOD by this method was 0.01 g mL^{-1} for melamine standard samples. Based on the intensity of the Raman spectra with vibration bands normalized by the band at 928 cm^{-1} (CH_2),the external standard method was employed for quantitative analysis. The linear regression (R^2) of the curve was 0.9998, the LOQ using this approach was 0.5 g mL^{-1} melamine in dairy product samples, the relative standard deviation was ≤ 10%, and the recoveries ranged from 93-109%. The test results for SERS were very precise and as good as those obtained by LC/MS/MS.

Our method is simple, quick (only requiring ~3 min), cost-effective, and sensitive for the detection of melamine in dairy product samples using a SERS liquid sensor. Therefore, Ag NPs are good candidates for melamine sensing and suitable for the detection of melamine in dairy products. We believe that liquid Au NPs and Ag NPs will be widely used as liquid sensing substrates and that SERS will be widely investigated and applied for the analysis of other molecules, including pesticides, herbicides, pharmaceutical chemicals, banned food dyes, explosives, nicotine, and organic pollutants.

Acknowledgements

We are grateful for financial support by the International Science and Technology Cooperation and Exchange Foundation (No. 2008DFA40270), a Strategic Eleventh-five-year Science and Technology Supporting Grant (No. 2009BAK58B01), and Special Funded Projects of the Fundamental Research Funds from the Chinese Academy of Inspection and Quarantine of China (Grant No. 2010JK017).

Author details

Mingqiang Zou, Xiaofang Zhang, Xiaohua Qi and Feng Liu

Chinese Academy of Inspection and Quarantine, China

References

[1] Abalde-Cela S., Ho S., Rodríguez-González B., Correa-Duarte M. A., Álvarez- Puebla R. A., Liz-Marzán L. M., Kotov N. A. (2009). Loading of Exponentially Grown LBL Films with Silver Nanoparticles and Their Application to Generalized SERS Detection.Angew. Chem. Int. Ed., vol. 48, pp. 1-5.

[2] Ai K. L., Liu Y. L., Lu L. H. (2009). Hydrogen-bonding recognition-induced color change of gold nanoparticles for visual detection of melamine in raw milk and ifrant formula.Journal of the American Chemical Society, vol. 131, pp. 9496-9497.

[3] Betz J. F., Cheng Y., Rubloff G. W. (2012). Direct SERS detection of contaminants in a complex mixture: rapid, single step screening for melamine in liquid infant formula. Analyst, vol. 137, pp. 469-470.

[4] Broszat M., Brämer R., Spangenberg B. (2008). A new method for quantification of melamine in milk by absorption diode-array thin-layer chromatography Planar J. Chromatogr., vol. 21, pp. 469-470.

[5] Campion A, Kambhampati P (1998). Surface-enhanced Raman scattering. Chem. Soc. Rev., vol. 4, pp. 241-250.

[6] Chen l., Liu Y. (2012). Ag-nanoparticle-modified single Ag nanowire for detection of melamine by surface-enhanced Raman spectroscopy. Journal of Raman Spectroscopy, vol. 43, pp. 986-991.

[7] Chen X., Parker S. G., Zou G., Su W., Zhang Q. J. (2010). ß-cyclodextrin-functionalized silver nanoparticles for the naked eye detection of aromatic isomers.ACS Nano, vol. 4, pp. 6387-6394.

[8] Cho M., Han, M. S., Ban C. (2008).Detection of mismatched DNAs via the dinding affinity of MutS using a gold nanoparticle-based competitive colorimetric method.Chemical Communications, vol. 38, pp. 4573-4575.

[9] Chu P., Mills D. (2008). Electromagnetic response of nanosphere paris: collective plasmon resonances, enhance field, and laser-induced force. Phys. Rev.vol. B77, pp. 45416-45416.

[10] Deiss F., Sojic N., White D. J., Stoddart P. R. (2010). Nanostructured optical fibre arrays for high-density biochemical sensing and remote imaging. Anal Bioanal Chem, vol. 396, pp. 53–71.

[11] Ehling S., Tefera S., Ho I. P., (2007).High-performance liquid chromatographic method for the simultaneous detection of the adulteration of cereal flours with melamine and related triazine by-products ammeline, ammelide, and cyanuric acid. Food Addit.Contam., vol. 24, pp. 1319-1325.

[12] Ellis D. I., Broadhurst D., Clarkeb S. J., Goodacre R. (2005).Rapid identification of closely related muscle foods by vibrational spectroscopy and machine learning.Analyst, vol. 130, pp. 1648-1654.

[13] Eric A. E., Garber J., (2008). Detection of melamine using commercial enzyme-linked immunosorbent assay technology.Food Prot., vol. 3, pp. 590-594.

[14] Guingab J. D., Lauly B., Smith B. W., Omenetto N., Winefordner J. D., (2007). Stability of silver colloids as substrate for surface-enhanced Raman spectroscopy detection of dipicolinic acid.Talanta, vol. 74, pp. 271-274.

[15] Guo L. Q., Zhong J. H., Wu J. M., Fu F. F., Chen G. N., Zheng X. Y., (2010). Visual detection of melamine in milk products by label-free gold nanoparticles.Talanta, vol. 82, pp. 1654-1658.

[16] Han C. P., Li H. B. (2010).Visual detection of melamine in infant formula at 0.1 ppm level based on silver nanoparticles.Analyst, vol. 135, pp. 583-588.

[17] Haynes C. L., McFarland A. D., VanDuyne R. P., (2005). Surface-Enhanced Raman Spectroscopy.Anal.Chem., vol. 77, pp. 338a-346a.

[18] He L., Liu Y., Lin M., Awika J., Ledoux D. R., Li H., Mustapha A., (2008). A new approach to measure melamine, cyanuric acid, and melamine cyanurate using surface-

enhanced Raman spectroscopy coupled with gold nanosubstrates. Sens. Instrumen. Food Qual., vol. 2, pp. 66-71.

[19] House P. G., Schnitzer C. S., (2008).SERRS and visible extinction spectroscopy of copper chlorophyllin on silver colloids as a function of Ph. J. Colloid Interface Sci., vol. 318, pp. 145-151.

[20] Jun B. H, Kim Noh G., Kang M. S, Kim H., Y. K, Cho M. H, Jeong D. H, Lee Y. S., (2011). Surface-enhanced Raman scattering-active nanostructures and strategies for bioassays.Nanomedicine, vol. 6, pp. 1463–1480.

[21] Kneipp K, Kneipp H., Itzkan I., Dasari R. R., Feld M. S., (1999). Ultrasensitive chemical analysis by Raman spectroscopy. Chem. Rev., vol. 99 (10): 2957-2976.

[22] Kneipp K., Haka A. S., Kneipp H., (2002). Surface-Enhanced Raman Spectroscopy in Single Living Cells Using Gold Nanoparticles.Appl. Spectrosc., vol. 56, pp. 150-154.

[23] Knoll W. (1998). Interfaces and thin films as seen by bound electromagnetic waves. Ann. Rev. Phys. Chem., vol. 49, pp. 569-638.

[24] Koglin E., Kip B. J., Meier R. J., (1996). Adsorption and Displacement of Melamine at the Ag/Electrolyte Interface Probed by Surface-Enhanced Raman Microprobe Spectroscopy.J. Phys. Chem., vol. 100, pp. 5078-5089.

[25] Küstner B., Gellner M., Schütz M., Schöppler F., Marx A., Ströbel P., Adam P., Schmuck C., Schlücker S., (2009). SERS Labels for Red Laser Excitation: Silica-Encapsulated SAMs on Tunable Gold/Silver Nanoshells. Angew. Chem. Int. Ed., vol. 48, pp. 1950-1953.

[26] Lee J. S., Lytton-Jean A. K. R., Hurst S. J., Mirkin C. A., (2007). Silver nanoparticle oligonucleotide conjugates based on DNA with triple cyclic disulfide moieties. Nano Letter, vol. 7, pp. 2112-2115.

[27] Lee P. C., Meisel D.,(1982).Adsorption and Surface-Enhanced Raman of Dyes on Silver and Gold Sols.J Phys.Chem., vol. 86, pp. 3391-3395.

[28] Leopold N., Lendl B., (2003).A New Method for Fast Preparation of Highly Surface-Enhanced Raman Scattering (SERS) Active Silver Colloids at Room Temperature by Reduction of Silver Nitrate with Hydroxylamine Hydrochloride.J. Phys. Chem. B, vol. 107, pp. 5723-5727.

[29] Li L., Li B. X. , (2009). Sensitive and selective detection of cysteine using gold nanoparticles as colorimetric probe.Analyst, vol. 134, pp. 14217-14226.

[30] Lin M., He L., Awika J., Yang L., Ledoux D. R., Li H., Mustapha A., (2008). Detection of Melamine in Gluten, Chicken Feed, and Processed Foods Using Surface-enhanced Raman Spectroscopy and HPLC.J. Food Sci., vol. 73, pp. 129-134.

[31] Medley C. D., Smith J. E., Tang Z., Wu Y., Bamrungsap S., Tan W. H. (2008). Gold nanoparticle-based colorimetric assay for the direct detection of cancerous cells.Analytical Chemistry, vol. 80, pp. 1067-1072.

[32] Meikun Fan, Gustavo F.S. Andrade, Alexandre G. Brolod. (2011). A review on the fabrication of substrates for surface-enhanced Raman spectroscopy and their applications in analytical chemistry.Analytica Chimica Acta, vol. 693, pp. 7–25.

[33] Micklander E., Brimer L., Engelsen S. B., (2002).Noninvasive Assay for Cyanogenic Constituents in Plants by Raman Spectroscopy: Content and Distribution of Amygdalin in Bitter Almond (Prunus amygdalus) .Appl. Spectrosc., vol. 56, pp. 1139-1146.

[34] Moskovit M, Dilella D. Maynard K., (1988). Surface Raman spectroscopy of a number of cyclic aromatic molecules adsorbed on silver: selection rules and molecular reorientation.,Langmuir, vol, 4, pp. 67-76.

[35] Muik B., Lendl B., Molina-Diza A., Ayora-canada M. J., (2003).Direct, reagent-free determination of free fatty acid content in olive oil and olives by Fourier transform Raman spectrometry. Anal.Chim.Acta., vol. 487, pp. 211-220.

[36] Mulvihill M., Tao A., Benjauthrit K., Arnold J., Yang P., (2008).Surface-enhanced Raman spectroscopy for trace arsenic detection in contaminated water.Angew. Chem.Int. Ed., vol. 47, pp. 6456-6460.

[37] Muniz-Valencia R., Ceballos-Magana S. G., Rosales-Martinez D., Gonzalo-Lumbreras R., Santos-Montes A., Cubedo-Fernandez-Trapiella A. R., Izquierdo-Hornillos C., (2008).Method development and validation for melamine and its derivatives in rice concentrates by liquid chromatography. Application to animal feed samples. Anal.Bioanal. Chem., vol. 392, pp. 523-531.

[38] Niikura K., Nagakawa K., Ohtake N., Suzuki T., Matsuo Y., Sawa H., (2009). Gold nanoparticle arrangement on viral particles through carbohydrate recognition: a non-cross-linking approach to optical virus detection. Bioconjugate Chemistry, vol. 20, pp. 1848-1852.

[39] Otto A. (2005).The 'chemical' (electronic) contribution to surface-enhanced Raman scattering. J Raman Spectrosc., vol. 36, pp. 497-509.

[40] Paradkar M. M., Irudayaraj J., (2001).Discrimination and classification of beet and cane inverts in honey by FT-Raman spectroscopy.Food Chem., vol. 76, 231-235.

[41] Peica N., Pavel I., Rastogi V. K., Kiefer W.,(2005).Vibrational characterization of E102 food additive by Raman and surface-enhanced Raman spectroscopy and theoretical studies.J. Raman Spectrosc., vol. 36, pp. 657-666.

[42] Rubayiza A. B., Meurens M., (2005). Chemical Discrimination of Arabica and Robusta Coffees by Fourier Transform Raman Spectroscopy. J. Agric. Food Chem., vol. 53, pp. 4654-4659.

[43] Tang H., Ng K., Chui S. S., Che C., Lam C., Yuen K., Siu T., Lan L. C., Che X., (2009). Analysis of melamine cyanurate in urine using matrix-assisted laser desorption/ionization Mass Spectrometry. Anal. Chem., vol. 81, pp. 3676-3680.

[44] Tian Z., Ren B., Wu D., (2002).Surface-enhanced Raman scattering: from noble to transition metals and from rough surfaces to ordered nanostructures J. Phys. Chem. B, vol. 106, pp. 9463-9483.

[45] Tiwari V.S., Oleg T., Darbha G.K., Hardy W., Singh J.P., Ray P.C., (2007). Non-resonance SERS effects of silver colloids with different shapes. Chem. Phys. Lett., vol. 446, 77-82.

[46] Varelis P., Jeskelis R., (2008). Preparation of [13C3]-melamine and [13C3]-cyanuric acid and their application to the analysis of melamine and cyanuric acid in meat and pet food using liquid chromatography-tandem mass spectrometry.Food Addit.Contam., vol. 25, 1208-1215.

[47] Wang H., Levin C. S., Halas N. J., (2005). Nanosphere Arrays with Controlled Sub-10-nm Gaps as Surface-Enhanced Raman Spectroscopy Substrates.J. Am. Chem. Soc. 127, 14992-14993.

[48] Wang Y. L., Li D., Ren W., Liu Z. J., Dong S. J., Wang E. K. (2008). Ultrasensitive colorimetric detection of protein by aptamer-Au nanoparticles conjugates based on a dot-blot assay. Chemical Communications, vol. 22, pp. 2520-2522.

[49] Wei W., Li S., Millstone J. E., Banholzer M. J., Chen X., Xu X., Schatz G. C., Mirkin C. A., (2009).Surprisingly long-range surface-enhanced Raman scattering (SERS) on Au–Ni multisegmented nanowires.Angew.Chem. Int. Ed., vol. 48, pp. 4210-4212.

[50] Weng Y. M., Weng R. H., Tzeng C. Y., Chen W. L., (2003). Structural analysis of triacylglycerols and edible oils by near-infrared Fourier transform Raman spectroscopy. Appl. Spectrosc., vol. 57, pp. 413-418.

[51] Wong H., Phillips D. L., Ma C., (2007). Raman spectroscopic study of amidated food proteins.Food Chem., vol. 105, 784-792.

[52] Yaffe N. R., Blanch E. W., (2008). Effects and anomalies that can occur in SERS spectra of biological molecules when using a wide range of aggregating agents for hydroxylamine-reduced and citrate-reduced silver colloids.Vib. Spectrosc., vol. 48, 196-201.

[53] Yang S., Ding J., Zheng J., Hu B., Li J., Chen H., Zhou Z., Qiao X., (2009). Detection of melamine in milk products by surface desorption atmospheric pressure chemical ionization Mass Spectrometry. Anal.Chem., vol. 81, pp. 2426-2436.

[54] Yu D., (2007).Formation of colloidal silver nanoparticles stabilized by Na^+–poly(γ-glutamic acid)–silver nitrate complex via chemical reduction process. Colloids Surf. B: Biointerfaces, vol. 59, pp. 171-178.

[55] Zhang J., Wang L. H., Pan D., Song S. P., Boey F. Y. C., Zhang H., (2008). Visual cocaine detection with gold nanoparticle and rationally engineered aptamer structures.Small, vol. 4, pp. 1196-1200.

http://dx.doi.org/10.5772/52485

[56] Zhang X., Zou M., Qi X., Liu F., Zhu X., Zhao B. (2010). Detection of melamine in liquid milk using surface-enhanced Raman scattering spectroscopy, J. Raman Spectrosc., vol. 41, pp. 1365–1370.

[57] Zhao B., Liu Z. L., Liu G. X., Li Z., Wang J. X., Dong X. T. (2009). Silver microspheres for application as hydrogen peroxide sensor. Electrochemistry Communications, vol. 11, pp. 1707-1710.

[58] Zhao W., Brook M. A., Li Y. F. (2008). Design of gold nanoparticle-based color-imetric biosensing assays. Chembiochem, vol. 9, pp. 2363-2371.

[59] Zhou Q., Li X., Fan Q., Zhang X., Zheng J.,(2006).Charge transfer between metal nanoparticles interconnected with a functionalized molecule probed by surface-enhanced Raman spectroscopy. Angew.Chem.Int. Ed., vol. 45, pp. 3970-3973.

IntechOpen

IntechOpen

IntechOpen