Food Chemistry 214 (2017) 25–31

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Highly sensitive determination of antimony in food by resonance Rayleigh scattering-energy transfer between grapheme oxide and I_3^-

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ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form 4 July 2016
Accepted 8 July 2016
Available online 9 July 2016

Keywords:
Sb
Hydride
Grapheme oxide
Silver nanorod
Rayleigh scattering energy transfer
SERS

ABSTRACT

Sb(III) was reduced to SbH_3 gas and introduced to the I_3^--grapheme oxide (GO) or I_3^--silver nanorod (AgNR)-Victoria blue B (VBB) solutions. Resonance Rayleigh scattering energy transfer (RRS-ET) occurred between the donor GO and the acceptor I_3^- due to the overlap between the absorption peak of I_3^- and RRS peak of GO. When I_3^- was reduced by SbH_3, RRS-ET weakened and the RRS intensity enhanced. The increased RRS intensity was linear to Sb concentration in the range of 2.1–376.6 μg/L. In the I_3^--AgNR-VBB solution, I_3^- combined with VBB to form VBB-I_3 and there was a weak surface-enhanced Raman scattering (SERS) effect. When SbH_3 reduced I_3^-, the SERS intensity increased due to the release of SERS active VBB. The enhanced SERS intensity was linear for Sb concentration in the range of 8.4–292.9 μg/L. The RRS-ET method was applied for determination of Sb in food with satisfactory results.

1. Introduction

Humans are exposed widely to antimony and its related compounds from flame retardant, alloy materials, electronics, glass, ceramics, polymerization catalysts and drugs. However, antimony is not an essential nutrient for human (Krachler & Emons, 2001) and many of its compounds are toxic, inhibiting enzyme activity. Therefore, determination of antimony content in foods is important. At present, the main analysis methods for determination of antimony are spectrophotometry (Rath, Jardim, & Dorea, 1997; Trivelin, Rohwedder, & Rath, 2006), atomic absorption spectrometry (AAS) (Denkhaus, Beck, Bueshler, Gerhard, & Golloch, 2001), atomic fluorescence spectrometry (AFS) (Gong, Zhang, & Shi, 2012), high performance liquid chromatography-atomic fluorescence spectrophotometry (HPLC-AFS) (Gregori, Quiroz, Pinochet, Pannier, & Potin-Gautier, 2005), and inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Waldo et al., 2011). The AAS method is simple, but its sensitivity is low. Combined with HPLC, atomic spectrometry has been used to improve sensitivity for the determination of antimony in foods. However, the required equipment is expensive and the process complex.

The hydride generation (HG) technique is often used to separate or concentrate analytes to improve the selectivity and sensitivity. It is the best way of introducing samples in the atomic spectral detection of hydride elements, such as As, Se, Bi, Ge, Sn, Pb, Sb, Te and Hg (Kumar & Riyazuddin, 2010; Zhang, Zeng, & Huang, 1991). RRS, using fluorescence spectrophotometry (Jamie, Yu, Larwasa, & Chen, 2014), is a simple and sensitive spectral technique, and has been applied to determination of trace analytes (Liang et al., 2015; Liu & Huang, 2013; Luo, He, et al., 2014; Luo, Wang, et al., 2013; Luo, Zhang, et al., 2014; Ma, Zhang, Liang, Liu, & Jiang, 2014; Shi, Luo, & Li, 2013; Wen, Liang, & Jiang, 2013; Wen, Luo, Liang, & Jiang, 2014). Recently, our research group combined HG technology with RRS molecular spectroscopy to establish new RRS spectral methods for determination of trace lead and selenium (Liang, Huang, Zhang, & Jiang, 2014; Liang, Wei, Wen, Yin, & Jiang, 2013). The resonance energy transfer (RET) principle has been applied in molecular spectroscopy of fluorescence, chemiluminescence and electroluminescence to develop fluorescence resonance energy transfer (FRET) (Qi et al., 2013; Yu et al., 2010), and other new technologies (Tang, Du, & Su, 2013). Gold nanoparticle RRS-ET has also been used for the determination of trace boron (Ye et al., 2014). Although some nanoparticles, including Au and Ag, have been used in RRS analysis, there are not many stable and water-soluble nanoparticles. Graphene oxide is one of the new nanomaterials with good water solubility and stability (He, Klinowski, Forster, & Lerf, 1998), and it can be used as the donor

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http://dx.doi.org/10.1016/j.foodchem.2016.07.050
0308-8146/

of RRS-ET. At present, GO has been used for RRS determination of human serum albumin (Wang, Xu, Wang, Liang, & Jiang, 2013). As far as we know, there are no reports describing coupling hydrides with the RRS-ET to determine trace antimony. In this paper, the I_3^--GO was used as a trapping solution, in which GO was used as donor and I_3^- as receptor, to set up a RRS-ET method set for determining trace antimony in food.

2. Materials and methods

2.1. Chemicals

A 0.837 mg/mL Sb(III) standard stock solution was prepared as follows. In a beaker, 0.100 g antimony trioxide (Shanghai Chemical Reagents Co., Shanghai, China) was dissolved in 30 mL concentrated hydrochloric acid, then transferred into a 100 mL volumetric flask and diluted to the mark with water. A 0.4 mmol/L I_3^- solution was prepared as follows. 3.32 g KI (Shanghai Chemical Reagents Co., Shanghai, China) was dissolved in water before 0.026 g I_2 (Shanghai Chemical Reagents Co., Shanghai, China) was adding and dispersing with ultrasonic bath. Then, it was diluted to 250 mL with water. Fresh 14.4 mg/mL $NaBH_4$ (Shanghai Chemical Reagent Co., Shanghai, China), 9 mol/L H_2SO_4, and 0.01% grapheme oxide (GO) (Wang et al., 2013) were used in the reduction of Sb(III). 10 mmol/L $AgNO_3$ (Sinopharm Chemical Reagent Beijing Co., Ltd, Beijing, China) and 30% H_2O_2 (Shanghai Chemical Reagent Co., Shanghai, China) was used in the preparation of nanoparticles. 50 μmol/L Victoria blue B (VBB) (Shanghai Chemical Reagent Co., Shanghai, China) and 1 mol/L NaCl (Shanghai Chemical Reagent Co., Shanghai, China) were prepared for the SERS method.

2.2. Preparation of red silver nanorod (AgNR)

Water (43 mL) was placed in a 100 mL conical flask on a magnetic stirrer, and 2 mL 10 mmol/L $AgNO_3$, 3 mL 60 mmol/L sodium citrate (Sinopharm Chemical Reagent Beijing Co., Ltd, Beijing, China), 480 μL 30% H_2O_2, and 800 μL 0.1 mol/L $NaBH_4$ (Sinopharm Chemical Reagent Beijing Co., Ltd, Beijing, China) added successively. The color changed from yellow to blue. Then, the solution was heated in a microwave oven for 90 s before being diluted to 50 mL with water to obtain a 43.1 mg/L Ag nanoparticle solution, which was red in color.

2.3. Sample pretreatment

10 g minced pig's liver or kidney, obtained from market, was placed in a porcelain crucible, carbonized in an electric cooker, and incinerated in a muffle furnace for about 120 min at 600 °C. Then, the white sample ash was dissolved by 10 mL 0.1 mol/L HCl and diluted to 50 mL with water.

2.4. Procedure

2.4.1. RRS system

An amount of Sb(III) standard solution and 200 μL 9 mol/L H_2SO_4 were added to the reaction bottle and diluted to 10 mL with water. In the absorption bottle, 300 μL 0.4 mmol/L I_3^- and 600 μL 0.01% GO or 300 μL 0.2% $HAuCl_4$ were added and diluted to 5 mL. The reaction bottle and absorption bottle were connected with rubber hose. A 10 mL 14.4 g/L $NaBH_4$ solution was added to the separating funnel. Under ultrasound, the funnel was opened, and $NaBH_4$ was added to the reaction flask. SbH_3 gas produced was introduced to the absorption solution. After 20 min, some of the absorption solution was transferred to a 1 cm quartz cell. The RRS spectra, RRS intensity I, and the blank (I_0) were recorded, and $\Delta I = I - I_0$ calculated.

2.4.2. SERS system

A certain amount of Sb(III) standard solution and 200 μL 9 mol/L H_2SO_4 were added to the reaction bottle and diluted to 10 mL with water. In the absorption bottle, 300 μL 0.4 mmol/L I_3^- was diluted to 5 mL. The reaction bottle and absorption bottle were connected with rubber hose. 14.4 g/L $NaBH_4$ (10 mL) was added to the funnel. Under ultrasound, the funnel was opened, and $NaBH_4$ was added to the reaction flask. The SbH_3 gas was introduced to the absorption solution. After the reaction, a 700 μL 43.1 mg/L AgNR, 200 μL 50 μmol/L VBB and 150 μL 1 mol/L NaCl were added into the absorption bottle and mixed well. Some of the absorption solution was transferred to a 1 cm quartz cell. The SERS spectra, SERS intensity at 1609 cm^{-1} (I) and the blank value (I_0) were recorded, and the $\Delta I = I - I_0$ was calculated.

3. Results and discussion

3.1. Analytical principle

In H_2SO_4, $NaBH_4$ reacted with H^+ to generate active hydrogen [H] that reduced Sb(III) to form SbH_3 gas, which was introduced to the I_3^--GO absorption solution with a large amount of H_2 as a carrier gas. There, I_3^- was reduced to I^- by SbH_3, which caused RRS intensity to increase due to the reduction in RRS-ET. With the increase in Sb (III) concentration, the concentration of I_3^- gradually decreased, and RRS intensity also increased linearly. Based on this principle, we established a hydride RRS-ET method for the determination of Sb (III) (Fig. 1A).

For the SERS analytical system, I_3^- reacted with the molecular probe VBB to form association complex particles that exhibited weak SERS activity. With the increase in Sb(III) concentration, the concentration of I_3^- gradually decreased, and SERS intensity also increased linearly. Thus, a hydride SERS method was established to determine Sb(III) with the label-free molecular probe of VBB (Fig. 1B).

3.2. RRS spectra

GO nanoparticles exhibited three RRS peaks at 280 nm, 322 nm and 370 nm, respectively. When GO coupled with I_3^-, RRS-ET occurred, and the system exhibited weak RRS peaks (Fig. 2a). With the increase in Sb(III) concentration, the concentration of I_3^- gradually decreased through a reduction in SbH_3, and the RRS peaks intensity gradually increased due to decrease in RRS-ET (Fig. 2b–2i). In this article, the most sensitive wavelength (322 nm) was selected for determination of Sb.

For the Au^{3+} trapping solution, Au^{3+} was reduced to generate gold nanoparticles (AuNPs) with two RRS peaks, at 374 nm and 549 nm (Fig. 3). With the increase in Sb(III) concentration, the RRS peaks intensity linear increased. In this article, 374 nm was selected for the determination of Sb.

For the I_3^--AgNR-VBB system, there was a strong RRS peak at 291 nm (Fig. S1). With the increase in Sb(III) concentration, the RRS peak intensity increased linearly. In this article, 291 nm was selected for the determination of Sb.

3.3. SERS spectra

Although some SERS quantitative methods and the AgNR substrate have been reported for detection of trace Hg(II), nitrite and β-agonist phenylethanolamine A (Jiang et al., 2014; Li et al., 2014; Liang et al., 2015; Luo, Wen, et al., 2014; Zhang et al., 2015), there are no reports about the coupling of the hydride reaction with SERS for the determination of antimony. In the trapping solutions, $HAuCl_4$ and I_3^--GO, there are no SERS peaks for the VBB