



A novel approach for simultaneous analysis of perchlorate (ClO_4^-) and bromate (BrO_3^-) in fruits and vegetables using modified QuEChERS combined with ultrahigh performance liquid chromatography-tandem mass spectrometry

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ABSTRACT

Perchlorate (ClO_4^-) and bromate (BrO_3^-) are mainly determined by ion chromatography methods. The present work aims to develop a modified QuEChERS combined with ultrahigh performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) method for simultaneous analysis of ClO_4^- and BrO_3^- in fruits and vegetables including cherry tomato, strawberry, tomato, potato, lettuce and pakchoi. Two target inorganic anions were separated on a Diamonsil C18(2) column by gradient elution, scanned in ESI negative mode and detected under multiple reactions monitoring (MRM). Limit of detection (LOD) and method limit of quantification (MLOQ), matrix effect, accuracy and precision of the developed method were investigated. Results were linear in their concentration ranges, with coefficients of determination (r^2) bigger than 0.999. LODs for ClO_4^- and BrO_3^- were 0.1 $\mu\text{g/L}$ and 0.5 $\mu\text{g/L}$, respectively. The validated method provided sufficient selectivity, sensitivity and accuracy to screen for ClO_4^- and BrO_3^- with ignorable matrix effects. Recoveries for different kinds of negative samples at 3 spiked levels were between 82.0% and 99.5%. Both intraday-precision and interday-precision were satisfactory, showing RSD_r values in the range of 2.1–7.1% and RSD_R values in the range of 7.2–10.8%. The proposed method was successfully applied to determine target inorganic anions in several fruits and vegetables. Perchlorate was detected in 12 vegetable samples with the concentrations ranged from 21 $\mu\text{g/kg}$ to 162 $\mu\text{g/kg}$. Results indicated that there was wide ClO_4^- contamination in vegetables, confirming its urgency for monitoring harmful inorganic anions in our daily consumed vegetables.

1. Introduction

Perchlorate (ClO_4^-), an inorganic anion, is highly soluble in water and persistent in the environment (Kumarathilaka, Oze, Indraratne, & Vithanage, 2016). It has gained significant attention in recent years due to its widespread occurrence in our surroundings (Krynitsky, Niemann, Williams, & Hopper, 2006). Perchlorate can disrupt thyroid function by competitively inhibiting the uptake of iodide, resulting in the decrease of thyroid hormones (Leoterio et al., 2017). Consequently, pregnant women, fetuses, infants, and people with thyroid disorders or iodine deficiency are particularly at risk to perchlorate exposure (Lin, Lo, & Fuh, 2012).

Perchlorate contamination was firstly discovered in the lower Colorado River in 1997 and the combination of natural processes and human activities resulted in the widespread presence of perchlorate in

water (Kumar et al., 2012), dust (Gan, Sun, Wang, & Deng, 2014), and soil (Tang et al., 2017). Unfortunately, several studies have shown that perchlorate can be rapidly captured and accumulated in leafy plants through contaminated soil or irrigation water (Dong, Xiao, Xian, & Wu, 2018; Jackson et al., 2005), resulting in elevated perchlorate concentration in agricultural products such as lettuce (Voogt & Jackson, 2010), spinach (Seyfferth & Parker, 2006), soybean sprouts (Yang & Her, 2011), and some other fruits and vegetables (Calderón, Godoy, Escudey, & Palma, 2017). The main pathway of perchlorate into the human body is through the ingestion of contaminated food. Thus, development of sensitive and robust methods for analysis of perchlorate in foods is of great importance.

Another inorganic anion, bromate (BrO_3^-), occurs in drinking water primarily as a disinfection by-product (West et al., 2015). Bromate is shown to be harmful to kidney, brain and other tissues and

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organs of human (Yan, Zhang, Yu, Liu, & Chen, 2016) and has been classified as a group 2B carcinogen at low levels by the International Agency for Research on Cancer (IARC) (Xian et al., 2017). The maximum allowable level of bromate in drinking water established by both the U.S. Environmental Protection Agency (EPA) and the World Health Organization (WHO) is 10 µg/L (Zhang et al., 2016). Unfortunately, recent studies have shown that bromate is presented not just in water, but in potato snacks (Arias et al., 2010), flour (Yan et al., 2016), bread and bread additives (Shi, Liang, Cai, & Mou, 2006), and other foods (Kim & Shin, 2012). Therefore, although many countries have prohibited or reduced the use of bromate in the food industry, there is also a need for development of analytical technologies for bromate analysis in foods.

At present, the mainly analytical methods used for analysis of perchlorate and bromate are X-ray fluorescence analysis (Hatzistavros & Kallithrakas-Kontos, 2011), electrophoresis (Takayanagi, Ishida, Mbuna, Driouch, & Motomizu, 2006), flow-injection analysis (Yan et al., 2016), ion chromatography (IC) in combination with different detection modes including conductivity detection (CD) (Wagner et al., 2006), mass spectrometry (MS) (Mathew, Gandhi, & Hedrick, 2005), inductively coupled plasma mass spectrometry (ICP/MS) (Shi & Adams, 2009) and tandem mass spectrometry (MS/MS) (Krynitsky et al., 2006; Wang et al., 2009), and gas chromatography-mass spectrometry (GC-MS) (Lim & Shin, 2012; Shin, 2012). However, the sensitivities of X-ray fluorescence analysis, electrophoresis and flow-injection analysis are not adequate to detect low µg/L (Zhang et al., 2016). IC-CD lacks selectivity and can lead to the reporting of false positives (El Aribi, Le Blanc, Antonsen, & Sakuma, 2006). IC-MS is vulnerable to be suffered from various interferences of cationic or anionic species in complex matrix analysis. It may only be suitable for analysis of simple matrix such as water (Hatzistavros & Kallithrakas-Kontos, 2011) and strong alkaline solution used in the mobile phase is easy to contaminate the mass spectrometry detector with respect to IC in combination with any MS analysis and thus decrease its life time (Xian et al., 2017). As for GC-MS, it involves multistep reactions including removal of free bromide and derivatization process (Shin, 2012).

Liquid chromatography-tandem mass spectrometry (LC-MS/MS) has been increasingly used in the analysis of complex matrix due to its excellent selectivity and anti-interference capability (Dong & Xiao, 2017; Dong, Zeng, & Bai, 2018; Xian et al., 2016). Previous literatures have reported the analysis of single perchlorate or bromate mainly in soil (Winkler, Minter, & Willey, 2004), water (Kim & Shin, 2012; Lin et al., 2012), and other foods (Arias et al., 2010) by LC-MS/MS. Nevertheless, the monotonous detection of target analytes restricted its wide application. To our best knowledge, no literatures have been reported for the simultaneous analysis of perchlorate and bromate in fresh fruits and vegetables by LC-MS/MS.

Therefore, the objective of the present work was to develop a selective, reliable ultrahigh performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) method for the simultaneous determination of ClO_4^- and BrO_3^- in fresh fruits and vegetables. The pretreatment extraction and QuEChERS purification were optimized and the established method was validated in terms of several parameters. Finally, the validated method was applied for the analysis of target inorganic anions in fruits and vegetables including tomato, cherry tomato, potato and leafy vegetables purchased from local markets in Guangzhou city, China. The research approach is shown in Supplemental Material Fig. S1.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.foodchem.2018.07.091>.

2. Materials and methods

2.1. Chemicals and reagents

HPLC grade acetonitrile was purchased from Merck (Darmstadt,

Germany). Formic acid (HPLC grade, purity: 99%) and ammonium acetate (HPLC grade, purity: 98%) were obtained from CNW Technologies GmbH (Düsseldorf, Germany). Primary secondary amine (PSA, 40–63 mm, 6 nm), graphitized carbon black (GCB) and octadecylsilane (C18) used as sorbents in QuEChERS technique were all purchased from CNW Technologies GmbH (Düsseldorf, Germany). Other chemicals and reagents used in the present work were of analytically pure and provided by Guangzhou Chemical Reagent Factory (Guangzhou, China). Ultrapure water (resistivity > 18.0 MΩ·cm) was used in the whole experiment.

2.2. Instruments

The UPLC-MS/MS system, consists of a Waters ACQUITY™ UPLC system and a Waters Xevo™ TQ tandem triple quadrupole mass spectrometer (Waters Corp., Beverly, MA), was applied for the separation and determination of target inorganic anions. A T25 high speed homogenizer (IKA GmbH, Germany) was employed for the mixing of the sample solution. Samples were vortex mixed with a MS3 basic vortex mixer (IKA GmbH, Germany). A KQ-250DV CNC ultrasonic cleaning device (Kunshan, China) was used for the supersonic-assisted extraction. Centrifugation of sample solution was accomplished by a 5418 high speed centrifuge (Eppendorf Corp., Germany). The R-210/215 rotary evaporator (Buchi Co., Switzerland) was applied for drying of the extraction solution. A Milli-Q ultrapure system (Millipore, Bedford, MA, USA) was used to prepare the ultrapure water.

2.3. Preparation of standard solutions

Standard solution (1000 mg/L) of perchlorate (ClO_4^- , purity: 100%), standard of potassium bromate (KBrO_3 , purity > 99.8%) were purchased from Sigma-Aldrich (St. Louis, USA). Standard stock solution (1000 mg/L) of bromate (BrO_3^-) was then prepared by accurate conversion and dissolving appropriate amounts of potassium bromate in water. The mixed standard solution (0.5 mg/L) of perchlorate and bromate was obtained by appropriate dilution of each standard stock solution with 50% acetonitrile water (v/v). All standard stock solutions and the mixed standard solution were immediately stored in a refrigerator at 4 °C. The required mixed standard working solutions were obtained by further dilution of the mixed standard solution with 50% acetonitrile water (v/v) prior to use.

2.4. Samples and sample preparation

Cherry tomato and 2 kinds of leafy vegetables (lettuce and pakchoi) were provided by Guangzhou Harmony Food Science and Technology Co., Ltd. (Guangzhou, China). Strawberry, tomato and potato were purchased from strawberry fields and markets located in Guangzhou city, China. A total of 34 fruits and vegetables samples were analyzed in the present work, including 2 cherry tomato samples, 6 lettuce samples, 6 pakchoi samples, 4 strawberry samples, 8 tomato samples and 8 potato samples.

Approximately 100 g of sample was minced and 1.0 g of which was accurately weighed into a clean 50 mL plastic centrifuge tube. 5 mL of 1% formic acid-acetonitrile (v/v) was added and the sample solution was mixed evenly. Another 5 mL of 1% formic acid-acetonitrile (v/v) was adopted for washing the homogenizer twice and then transferred into the above centrifuge tube. After that, the mixed sample solution was vortexed for 2 min and ultrasonic-assisted extracted for 20 min. The dispersed sample solution was vortexed again and subsequently centrifuged at 8000 r/min for 5 min. The supernatant was then transferred to a clean 15 mL glass colorimetric tube and dried by mild nitrogen stream in a 40 °C water-bath. 1 mL of 1% formic acid–water (v/v) was added and mixed evenly. After that, the above solution was purified by modified QuEChERS technique described as follow: sample solution was moved to a 2.5 mL high speed plastic centrifuge tube which

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