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Analytical Methods

Magnetic graphene sol–gel hybrid as clean-up adsorbent for acrylamide analysis in food samples prior to GC–MS

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ABSTRACT

Graphene (G) modified with magnetite (Fe_3O_4) and sol–gel hybrid tetraethoxysilane-methyltrimethoxysilane (TEOS-MTMOS) was used as a clean-up adsorbent in magnetic solid phase extraction (MSPE) for direct determination of acrylamide in various food samples prior to gas chromatography-mass spectrometry analysis. Good linearity (R^2 = 0.9990) was achieved for all samples using matrix-matched calibration. The limit of detection (LOD = 3 × *SD*/*m*) obtained was 0.061–2.89 μg kg^{-1} for the studied food samples. Native acrylamide was found to be highest in fried potato with bright-fleshed (900.81 μg kg^{-1}) and lowest in toasted bread (5.02 μg kg^{-1}). High acrylamide relative recovery (RR = 82.7–105.2%) of acrylamide was obtained for spiked (5 and 50 μg kg^{-1}) food samples. The Fe_3O_4@G-TEOS-MTMOS is reusable up to 7 times as a clean-up adsorbent with good recovery (>85%). The presence of native acrylamide was confirmed by mass analysis at *m*/*z* = 71 ($[C_3H_5NO]^+$) and *m*/*z* = 55 ($[C_3H_3O]^+$).

1. Introduction

Acrylamide (2-propendiamide) is a carcinogenic substance with high toxicity that is classified in group 2A according to international agency for research on cancer (IARC, 1994). It is found in carbohydrate-rich cooked food under high temperature heating (Russo, Avino, Centola, Notardonato, & Cinelli, 2014). Acrylamide with low molecular weight and high solubility in water easily passes through the soil ground water (Riboldi, Vinhas, & Moreira, 2014) and also biological systems, which binds to thiols and protein that causes epigenetic and mutagenic effects respectively (Besaratinia & Pfeifer, 2007). IARC reported that 0.03 mg kg^{-1} of acrylamide is suspected as human carcinogen (IARC, 1994) and the residual allowance concentration for acrylamide monomer in drinking water is 0.1 μg kg^{-1} as set by the European Commission (EC) 98/83/EC (EC, 1998). The presence of acrylamide in food sample was first reported in 2002 by Swedish scientists, that acrylamide could be formed easily in fried carbohydrate-rich foods from 5 to 4.000 μg kg^{-1}, it was not detected in boiling food or unheated food (Tareke, Rydberg, Karlsson, Eriksson, & Törnqvist, 2002). Thereafter, Joint FAO/WHO expert committee on food additives (JECFA/64/SC) reported the mean concentration 16 μg kg^{-1} for potato puree/mashed/boiled and 752 μg kg^{-1} for potato crisps (JECFA., 2005).

Sample preparation procedures for acrylamide analysis include homogenization, addition of internal standards, defatting, extraction, concentration and clean-up process (Elbashir, Omar, Wan Ibrahim, Schmitz, & Aboul-Enein, 2014). Due to complex matrices of food samples, clean-up process is often necessary for acrylamide analysis prior to instrument analysis. Different chromatographic instruments are used for acrylamide detection such as high performance liquid chromatography with ultraviolet detector (HPLC-UV) (Wang, Feng, Guo, Shuang, & Choi, 2013), gas chromatography-mass spectrometry (GC–MS) for direct determination of acrylamide (Dunovská, Cajka, Hajslová, & Holadová, 2006; Omar, Wan Ibrahim, & Elbashir, 2014; Xu et al., 2013b), liquid chromatography tandem mass spectrometry (LC-MS/MS) for direct analysis with large volume injection (Backe, Yingling, & Johnson, 2014;

Abbreviations: TEOS-MTMOS, tetraethoxysilane-methyltrimethoxysilane; QuEChERS, quick easy cheap effective rugged and safe; RP-MSPE, reverse phase magnetic solid phase extraction; GC-MS, gas chromatography mass spectrometry; JECFA, Joint Expert Committee on Food Additives; FAO, Food and Agriculture Organization; WHO, World Health Organization.

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Liu, Zhao, Yuan, Chen, & Hu, 2008), LC-MS (Anese, Suman, & Nicoli, 2010) and gas chromatography with electron capture detector (GC-ECD) (Russo et al., 2014). The HPLC-based technique provides unsuitable retention time for high polar acrylamide (Backe et al., 2014), but GC-based techniques, particularly with polar columns (e.g. CarboWax), shows good retention time (Omar et al., 2014). Hence, the response of the instrument directly depends on sample preparation or cleaning-up processes.

Solid phase extraction (SPE) is the most popular sample preparation method with potential benefits i.e., high breakthrough volume and it improved sample handling time (Bagheri & Banihashemi, 2015). SPE is an interesting method that has been used for acrylamide preconcentration, enrichment and clean-up processes (Longhua, Limin, Xuguang, Zhixiang, & Jiaming, 2012; Nielsen, Granby, Hedegaard, & Skibsted, 2006; Wang et al., 2013). Different types of materials have been successfully used as SPE sorbents for acrylamide analysis i.e., graphitized black carbon (Tareke et al., 2002), primary secondary amine (PSA) (Dunovská et al., 2006; Wenzl, Lachenmeier, & Gökmen, 2007), Oasis HLB (Wang et al., 2013) and C18 (Longhua et al., 2012).

Recently, different methods as mentioned above have been successfully used for acrylamide analysis. Although, these techniques/methods have potential benefits, but they still have several drawbacks. For instance, isotope dilution or the use of isotope as an internal standard prior to MS analysis provides high cost (Dunovská et al., 2006; Nielsen et al., 2006), addition of Carrez reagents (I, II) prior to GC analysis increase water interference that is harmful to GC columns (Gökmen et al., 2005; Senyuva & Gökmen, 2005), acrylamide derivatization (e.g. bromine and D-cysteineandtrifluoroacetate) prior to chromatographic analysis (Lim & Shin, 2014; Russo et al., 2014; Zhang, Ren, Zhao, & Zhang, 2007), long and tedious process (acrylamide silanation/derivatization) is an essential in order to obtain volatile compounds prior to solid phase microextraction (SPME) (Lagalante & Felter, 2004), reduction of acrylamide (Zhang, Huang, Wang, & Cheng, 2015) and degradation via Hofmann reaction (Liu et al., 2014). These procedures can cause higher cost, longer cleaning-up time, tedious, hazardous bromine handling and production of secondary contaminants. SPME with CW-DVB has also been used for acrylamide analysis (Lee, Chang, & Dou, 2007) but SPME is less robust compared to RP-MSPE as the fibre tends to break easily. The need to purchase SPME fibres and holder is more costly compared to the mere use of the RP-MSPE material (involve mere addition to sample matrix) which is more attractive.

Omar et al. (2014) stated the application of QuEChERS (quick, easy, cheap, effective, rugged and safe) method as a clean-up method for acrylamide analysis prior to GC–MS. The work focused on dispersive solid phase extraction (d-SPE) method based on sol–gel hybrid material, methyltrimethoxysilane-tetraethoxysilane (MTMOS-TEOS) as sorbent.

However, in the current study, a new method based on reversed phase magnetic solid phase extraction (RP-MSPE) using magnetite (Fe_3O_4 nanoparticles), graphene and sol–gel hybrid TEOS-MTMOS to produce Fe_3O_4@G-TEOS-MTMOS was used for clean-up in direct acrylamide analysis. Hence, the aim of the work is to develop a RP-MSPE method for the first time to enhance clean-up of the complex matrices of QuEChERS process prior to direct acrylamide determination in food samples. Incorporation of Fe_3O_4 nanoparticles provides fast extraction using an external magnet without the need for further centrifugation and filtration process. Graphene, is highly hydrophobic with high surface area, chemically stable and possess large π-stacking system. Thus, graphene shows high adsorption capacity and strong affinity towards non-polar compounds but does not adsorb highly polar acrylamide (clean-up matrix). Sol-gel hybrid TEOS-MTMOS as mesopores material with huge silica network also provided good clean-up ability prior to acrylamide analysis based on our published work (Omar et al., 2014). Incorporation of magnetite and graphene to TEOS-MTMOS thus is expected to ease separation process and clean-up more effectively. Fe_3O_4@G-TEOS-MTMOS has been previously synthesised, characterized and for the first time used for simultaneous analysis of polar and non-polar organophosphorus pesticides from water samples using solid phase extraction (Nodeh, Wan Ibrahim, Kamboh, & Sanagi, 2017). Eight different types of food samples namely fried potato with bright-fleshed, fried sweet purple and orange potato, potato chips, fried eggplant, fried banana, toast bread, and cheese snacks were examined for the presence of acrylamide. The RP-MSPE based on Fe_3O_4@G-TEOS-MTMOS has been applied to clean-up the complex matrices (eg. food colors) within a short time (Fig. 1) prior to direct acrylamide analysis using GC–MS. The outstanding analytical performances obtained proved that the Fe_3O_4@G-TEOS-MTMOS RP-MSPE method is an efficient clean-up method compared to MTMOS-TEOS dSPE and PSA-d-SPE methods (Omar et al., 2014), SPE clean-up with GC–MS analysis (Franek, Rubio, Diblikova, & Rubio, 2014 and SPE-clean-up using HLB Oasis with LC-GC–MS/MS analysis (Lee et al., 2013).

2. Material and methods

2.1. Standards, materials and reagents

Standard acrylamide (purity >99.8%) was purchased from Sigma Aldrich (St. Louis, MO, USA). HPLC grade methanol and AR grade acetone, ethyl acetate and ethanol (97%) were obtained from QReC (Selangor, Malaysia). HPLC grade acetonitrile and *n*-hexane were acquired from Merck (Schuchardt, Germany).

Acrylamide standard stock solution (1000 mg L^{-1}) was prepared in HPLC grade methanol and kept in a dark container and refrigerated until further analysis. The solution was prepared by dissolving 10 mg of acrylamide in HPLC grade methanol in a 10 mL volumetric flask and made up to the designated mark with methanol. It was diluted with methanol and water to produce standard calibration curve (10–1000 mg L^{-1}) and matrix- matched calibration curve (0.2–100 μg kg^{-1}), respectively. All the food samples used were purchased from a local market in Skudai, Johor Bahru, Malaysia.

2.2. Preparation of magnetic graphene-based hybrid sol–gel material

The magnetic material based on graphene modified with magnetite and sol–gel hybrid tetraethoxysilane-methyltrimethoxysilane (Fe_3O_4@G-TEOS-MTMOS) was used as reported in previous work (Nodeh et al., 2017). Briefly, graphene was obtained from graphite and magnetized (Fe_3O_4@G) as in previous study. Hence, the Fe_3O_4@G-TEOS-MTMOS obtained was by addition of 100 mg of Fe_3O_4@G into 30 mL of methanol-water (1:30) mixture followed by sonication for 30 min. Thereafter, TEOS (1 mL) and MTMOS (2 mL) were added into the methanol-water mixture, followed by dropwise addition of 1.5 mL ammonia solution. The solution was stirred for 15 min until it turns into a black gel. The black gel was left at room temperature for 2 days, then washed with excess water and methanol, and oven dried at 80 °C for 24 h.

2.3. Sample preparation

2.3.1. Potato samples

Potatoes with bright-fleshed, sweet purple and orange potato samples were cut (with skin) into small square pieces and 50 g of sample was fried in 10 g of edible oil (Sunflower Oil, purchased from local market) separately under kitchen stove for 10 min. For non-fried sample, potato was boiled in water for 30 min.

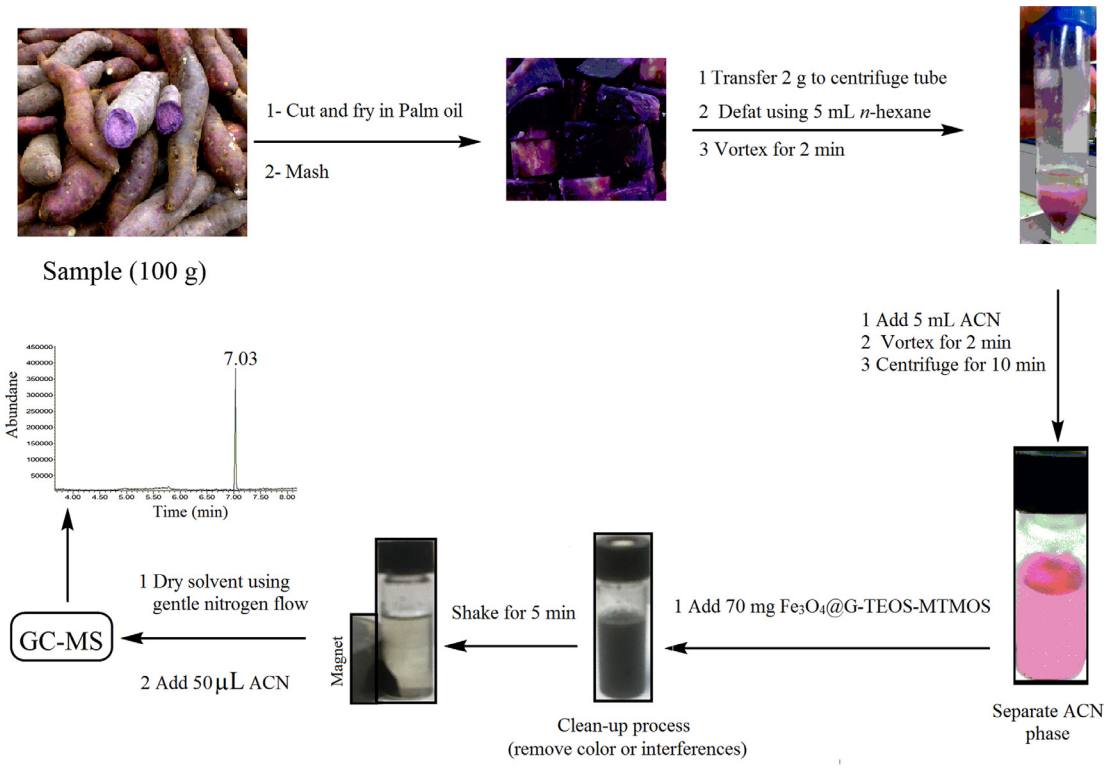

Fig. 1. Schematic process of solid–liquid extraction and Fe_3O_4@G-TEOS-MTMOS RP-MSPE clean-up process (test sample is purple sweet potato).

2.3.2. Fried eggplant

For eggplant samples, the skin was first removed, and then the flesh was cut using a knife into small square pieces (50 g) before fried in 10 g of sunflower oil for 10 min.

2.3.3. Fried banana, potato chips and cheese snack

Fried banana and potato chips and snack cheese samples were purchased from a local market in Skudai, Johor Bahru, Malaysia.

2.3.4. Toasted bread

A packet of bread was bought from a local market in Skudai, Johor Bahru, Malaysia and was toasted for 3 min using a home kitchen toaster before analysis.

All sample preparation was performed once.

2.4. Optimization of sample preparation process

Effective parameters on the extraction (extraction solvents, volume of solvent, volume of *n*-hexane (as defatting agent), mass of food samples, extraction time) and clean-up (mass of adsorbent, and clean-up time) performance were optimized. In this section, toasted bread was selected as test sample for the optimization of sample preparation processes. Initially, 2 g of toasted bread sample, 2 mL *n*-hexane, 2 mL acetonitrile, 10 mg adsorbent and 20 min clean-up time were used. Parameter was changed one at a time keeping the other parameters constant. The extraction optimization processes were performed using different solvents (methanol, acetone, acetonitrile and ethyl acetate), different solid-liquid extraction time (1–30 min) and different clean-up time (1–20 min). Finally, the optimized conditions were applied for further analysis.

2.5. Solid-liquid extraction and magnetic solid phase clean-up procedures

These procedures were carried out at optimized conditions (1 g food sample, 5 mL ACN as extraction solvent, 2 min extraction time, 5 min clean-up time and 70 mg adsorbent). Homogenized sample (1 g) was transferred into a 15 mL centrifuge tube and 100 μL of acrylamide was added (standard solution is 50 ng mL^{-1} of acrylamide) to give 0.5 μg kg^{-1} of AA. The samples were placed in refrigerator overnight until the acrylamide diffuse completely into the food samples. Then, 5 mL *n*-hexane was added for defatting process, followed by 2 min of vigorous mixing using a Heidolph vortex shaker (Schwabach, Germany). In order to extract acrylamide from the food samples, 5 mL of acetonitrile (ACN) was added, then vortexed for 2 min, and later centrifuged in a KUBOTA 2420 centrifuge (Tokyo, Japan) at 4000 rpm for 10 min. Two phases were observed; *n*-hexane phase include fat (top layer) and ACN phase (pinkish colored solution), which contained the extracted acrylamide and other soluble components most probably anthocyanins (down layer). The *n*-hexane layer was discarded and the ACN phase was pipetted, then filtered through a 0.45 μm nylon syringe filter (Croydon, Surrey) into a 10 mL glass vial. Then, 70 mg of the Fe_3O_4@G-TEOS-MTMOS adsorbent was then added for clean-up purposes, followed by shaking Heidolph vortex for 5 min (clean-up time). The adsorbent was collected using an external magnet. Then, 4 mL of the cleaned colorless ACN extract was transferred into another glass vial and evaporated to dryness under a gentle stream of nitrogen gas. The residue was reconstituted with 50 μL ACN and 1 μL of the reconstituted extract was injected into GC–MS. Triplicate GC–MS injections were performed. Fig. 1 shows the schematic process of solid-liquid extraction (SLE) and RP-MSPE clean-up process, in which the Fe_3O_4@G-TEOS-MTMOS adsorbent fully removed the food color to produce a clear solution. All RP-MSPE was performed in triplicates. Control samples were unspiked sample of each food analysed.

Due to high polarity and small size of acrylamide, it was not adsorb on the hydrophobic graphene-based adsorbent and fully remained in the ACN phase. Therefore, matrix (i.e. colour and interferences) adsorbed on the Fe_3O_4@G-TEOS-MTMOS adsorbent to give a clear extract solution.

2.6. Gas chromatography-mass spectrometry parameters and conditions

An Agilent 7890A GC system equipped with an Agilent 5975C Series MSD from Agilent Technologies, Inc. (Santa Clara, CA, USA) was used for acrylamide determination. An Agilent HP-CarboWax capillary (30 m length × 250 μm I.D., 0.25 μm d_f film thickness) was used as the GC column. Helium was used as a carrier gas with a flow rate of 1.0 mL min^{-1}. The injector and detector temperature were set at 250 °C and 280 °C, respectively. The oven temperature program started from 60 °C and ramped up to 200 °C (hold for 1 min) at 15 °C min^{-1}. Samples (1 μL) were injected into the injection port in splitless mode. Mass detector was operated in electron impact ionization (EI) mode at 70 eV. Selected ion monitoring (SIM) mode was used for monitoring of two main molecular ions (fragments) for acrylamide confirmation; $[C_3H_5NO]^+$ and $[C_3H_3O]^+$ at *m*/*z* 71 and *m*/*z* 55, respectively.

2.7. Matrix matched calibration

The proposed MSPE method was calibrated using matrix matched calibration technique. For this, standard solution of acrylamide (1–100 ng mL^{-1}) was spiked in aliquot of the food samples to give 0.2–100 μg kg^{-1}. The analytical performances of acrylamide analysis prior to GC–MS, were evaluated with different figure of merit parameters such as linearity, limit of detection (LOD), limit of quantification (LOQ), precision (repeatability and reproducibility) as measured by % RSD% and accuracy (recovery) under the optimized conditions.

2.8. Acrylamide recovery

The clean-up recovery processes was performed by spiking each food samples analysed. The food samples (1 g) were spiked with 100 μL and 1000 μL of acrylamide standard solution (50 ng mL^{-1}) to give 5 and 50 μg kg^{-1} of acrylamide in food samples. A volume of 5 mL ACN was used as the extractions solvent (QuEChERS solvent). The procedure was conducted as described in Section 2.4. Three replicate extractions were performed for each recovery level. Due to the presence of acrylamide in the food samples analysed, percentage relative recovery (% *RR*) was used as in Eq. (1).

$$\%RR = \left(\frac{C_{found} - C_{real}}{C_{spiked}}\right) \times 100 \quad (1)$$

where C_{found} is the acrylamide concentration in final solution (after clean-up), C_{real} is the native acrylamide concentration in food samples without the addition of acrylamide standard solution, and C_{spiked} is the added concentration of acrylamide in food samples.

3. Results and discussion

3.1. Extraction and clean-up optimization process

3.1.1. Types of extraction solvent and volume

In order to choose the best solvent for acrylamide extraction from the food samples, different polar solvents were examined for highly polar acrylamide. Polar protic and aprotic solvents namely methanol, ethanol, ethyl acetate, acetone and acetonitrile (ACN) were examined. The result showed that the highest % relative recovery was observed for polar ACN, thus it was used as the partition solvent for further analysis. ACN reportedly used for AA extraction from food samples (Liu et al., 2014).

In order to improve the extraction efficiency, the volume of ACN was examined from 1–10 mL. The volume of solvent used must be sufficient to extract all the analytes (acrylamide). The highest recovery of acrylamide was obtained with 5 mL of ACN, which was selected for further analysis.

3.1.2. Volume of defatting solvent

Due to the complex matrix of food samples and also the presence of excess oil in the frying stage, fat removal is necessary. In survey of literatures, *n*-hexane is the best candidate as a defatting agent, this probably due to hydrophobic interaction (Dunovská et al., 2006; Fernandes & Soares, 2007; Omar et al., 2014). Furthermore, the optimization of *n*-hexane volume is important to fully remove fat and produce a clean matrix. Volumes of *n*-hexane tested were from 1 to 10 mL. It was observed that 5 mL *n*-hexane gave the highest recovery of acrylamide and thus selected for further analysis (conditions: 2 g food sample (spiked 1 μg mL^{-1}), 5 mL ACN, 10 min extraction time).

3.1.3. Extraction time

The effect of different extraction time was investigated for acrylamide extraction from 2 g of food sample (spiked with 5 μg kg^{-1} of acrylamide and 5 mL ACN as desorption solvent), f by varying extraction time in the range of 0.5–30 min at room temperature. As the extraction time increased, the peak area of acrylamide also increased since more acrylamide was transferred from food sample (solid phase) into ACN phase (liquid phase). This trend increase continuously until 2 min, and then the peak area became slightly stable. Thus, 2 min was chosen as the optimum extraction time for acrylamide partition.

3.1.4. Amount of food sample

In QuEChERS method, the amount of solid samples (e.g. food, soil and fruits) play a main role in extraction efficiency. Different amount of food samples (0.5–10 g) spiked with acrylamide (5 μg kg^{-1}) then were distributed and treated with 5 mL ACN and 2 min extraction time. As the amount of sample increased from 0.5 g to 1 g, the recovery increased significantly from 62.25% to 88.9%, and increased slightly until 5 g. Since the increase in acrylamide recovery was not significant on increasing the food samples from 1 g to 5 g, thus, 1 g of food sample was selected as the optimum amount for the further analysis.

3.1.5. Clean-up time using RP-MSPE

The effect of clean-up time was investigated by studying different shaking times (1–30 min) using 70 mg Fe_3O_4@G-TEOS-MTMOS adsorbent. The % relative recovery (%RR) was found to be highest (>90%) at 5 min shaking time and also the food color was fully removed (see Fig. 1). Thus, 5 min was used as the optimum clean-up time for further analysis process.

3.1.6. Mass of Fe_3O_4@G-TEOS-MTMOS in RP-MSPE

Dispersive clean-up process was carried out using different mass of Fe_3O_4@G-TEOS-MTMOS adsorbent. Due to hydrophobic affinity of graphene-based adsorbent and high porosity of sol–gel TEOS-MTMOS, interferences were most probably attached on the (possible interactions: π-π interaction, H-bonding and electrostatic attraction) adsorbent and highly polar acrylamide remain in solution. The mass of Fe_3O_4@G-TEOS-MTMOS in RP-MSPE were examined in the range 5 to 100 mg. It was found that the acrylamide recovery increased until 70 mg of adsorbent mass, and became slightly stable afterwards (results not shown). Thus, 70 mg adsorbent was used for further analysis.

3.2. Method validation

The efficiency of the target analytes may be affected due to the complexity of the solid matrices. Thus, in the current study matrix-matched calibration was used for quantification purpose using optimum conditions: 1 g food sample, 5 mL ACN as desorption solvent, 2 min extraction time, 5 min clean-up time and 70 mg adsorbent at different concentrations of acrylamide (0.2–100 μg kg^{-1}) were spiked in aliquot of the food samples. The analytical performances of acrylamide analysis prior to GC–MS, were evaluated with different figure of merit parameters such as linearity, LOD, LOQ, precision (repeatability and reproducibility) and accuracy (recovery) under the optimized conditions. The results obtained from the Fe_3O_4@G-TEOS-MTMOS RP-MSPE-were compared with MTMOS-TEOS d-SPE and PSA d-SPE as reported in our previous work (Omar et al., 2014).

Table 1 shows the analytical performances; the linearity was obtained in the range from 0.2 to 100 μg kg^{-1} for all food samples using the Fe_3O_4@G-TEOS-MTMOS adsorbent. The linearity started from 0.2 μg kg^{-1} for clean matrices (low fat) such as toasted bread and boiled potato, while for complex matrices (e.g. purple sweet potato and fried banana), the linearity started from 10 μg kg^{-1}, which was 100× higher than the clean matrices. However, linearity was 5× lower than TEOS-MTMOS d-SPE-and PSA d-SPE that were reported in our previous work (Omar et al., 2014).

LOD was calculated using the following equation: $LOD = \left(\frac{3\times SD}{m}\right), n = 3$ (Kaykhaii & Abdi, 2013), where SD ($n = 3$) is the standard deviation of the lowest concentration and m is the slope of the matrix matched calibration curve. The LOD (0.061–2.89 μg kg^{-1}) obtained for Fe_3O_4@G-TEOS-MTMOS RPMSPE method (Table 1), was 150× lower than the TEOS-MTMOS d-SPE (9.1–12.8 μg kg^{-1}) and PSA d-SPE (9.3–12.6 μg kg^{-1}) methods that were reported in our previous work (Omar et al., 2014). The LOQ was calculated using $LOQ = 3.3 \times LOD$. The proposed Fe_3O_4-G-TEOS-MTMOS RP-MSPE exhibited LOD that is 1.5× and 50× well below the carcinogenic level (set by IARC, 1994) allowance of acrylamide in food samples and water samples, respectively.

The repeatability and reproducibility of the Fe_3O_4@G-TEOS-MTMOS RP-MSPE method were investigated by intra- and interday precision (%RSD) analysis. Good %RSD was obtained for intraday (1.3–6.8%, $n = 3$) and interday (4.9–10.1%, $n = 12$) precision for the extraction of 100 μg kg^{-1} of acrylamide from 1 g food sample. As a result, the obtained intraday precision (%RSD) from Fe_3O_4@-G-TEOS-MTMOS RP-MSPE is comparable to the %RSD of d-SPE MTMOS-TEOS (1.2–6.0%) and d-SPE PSA (1.6–4.2%). In contrast, interday %RSD for Fe_3O_4-@G-TEOS-MTMOS RP-MSPE was slightly higher than TEOS-MTMOS d-SPE (3.7–3.6%) and PSA d-SPE (2.6–6.0%), which is probably due to the low concentration of acrylamide (5 μg kg^{-1}) that was used in the current study compared to our previous work (600 μg kg^{-1}) (Omar et al., 2014).

The reusability of the Fe_3O_4-@G-TEOS-MTMOS was examined using 12 times clean-up process. After each clean-up process, the adsorbent was washed and alternatively used for the next extraction. Solvent volume of 2 mL methanol followed by 2 mL ACN solvents were used for washing to remove any interferences that were adsorbed on the adsorbent. The reusability of the Fe_3O_4-@G-TEOS-MTMOS was at least 4 times with recovery >90% and 7 times with recovery >85%.

3.3. Monitoring of native acrylamide in real food samples

Determination of native acrylamide in real samples was investigated in unspiked food samples under optimum conditions of Fe_3O_4@G-TEOS-MTMOS RP-MSPE method. The results are listed in Table 2. The highest value of acrylamide was found in fried potato with bright-fleshed (900.81 μg kg^{-1}) and the lowest was observed in toasted bread (5.02 μg kg^{-1}) (Table 2). The measured acrylamide level was well within the range of 64–5000 μg kg^{-1} as reported in fried potato samples (Hasegawa et al., 2007; Lim & Shin, 2014; Omar et al., 2014; Russo et al., 2014; Wang et al., 2013). Acrylamide in fried sweet orange and sweet purple potato was much lower than fried potato with bright-fleshed. To the best of our knowledge there was not found analytical data in the literature for fried sweet orange and purple potato. Acrylamide found in potato chips (192.98 μg kg^{-1}) was in the concentration range of 120–1500 μg kg^{-1} as reported previously (Mogol & Gökmen, 2014). The acrylamide in eggplant (133.45 μg kg^{-1}) was lower than that of our previous work (338 μg kg^{-1}) (Omar et al., 2014). Also, the measured acrylamide in toasted bread and banana chips was below the reported concentration range of 11–87 μg kg^{-1} (Mogol & Gökmen, 2014) and 28.9–243.7 μg kg^{-1} (Selamat, Sarker, & Lioe, 2010). The measured acrylamide in cheese snack (112.9 μg kg^{-1}) was higher than in corn snack (75 μg kg^{-1}) (Gruber et al., 2003).

In order to investigate the accuracy (recovery) of the proposed method, each food samples were spiked at two concentration levels of acrylamide of 5 μg kg^{-1} and 50 μg kg^{-1} in the calibration linearity range. These results are listed in Table 2. Good recoveries (87.31–105.97%) were obtained for all spiked samples.

3.4. Comparison of acrylamide before and after clean-up process

Fig. 2 shows a typical chromatogram (selective ion monitoring (SIM) mode) of acrylamide extraction from cheese snacks, followed by clean-up process using Fe_3O_4@G-TEOS-MTMOS. Fig. 2A and B shows spiked (50 μg kg^{-1}) chromatogram of acrylamide for cheese snack after and before clean-up process, respectively. It was clearly observed that 5 peaks (Fig. 3B) were removed after the clean-up process, and the peak area of acrylamide (AA) also increased. Fig. 2C and D shows the chromatogram of acrylamide for unspiked

Table 1
Analytical performance of Fe_3O_4@G-TEOS-MTMOS RP-MSPE for acrylamide analysis in different food samples.

Sample	Fe_3O_4@G-TEOS-MTMOS RP-MSPE and GC–MS analysis					
	Linearity (μg kg^{-1})	Equation	R^2	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	%RSD ($n = 3$)
Boiled potato	0.2–100	3848.9x + 1293.6	0.9988	0.061	0.200	0.8–2.1
Fried potato with bright-fleshed	1–200	4004.6x + 793.82	0.9986	0.243	0.812	2.3–5.7
Fried purple sweet potato	10–100	2814.2x + 5938.4	0.9984	2.32	7.75	3.5–6.1
Fried orange sweet potato	1–100	3105.5x + 1125.9	0.9973	0.277	0.926	2.3–4.1
Potato chips	1–100	2867.7x + 3132.3	0.9979	0.243	0.813	1.5–3.9
Fried eggplant	10–100	2845.6x - 153.12	0.9959	2.895	9.641	3.1–4.8
Toasted Bread	0.2–100	2834.6x - 3405.1	0.9989	0.062	0.208	0.8–3.8
Fried banana	10–100	2915.4x + 3855.1	0.9957	2.67	8.901	2.2–5.3
Cheese Snack	1–100	2674.4x + 3549.6	0.9970	0.279	0.931	3.2–5.7

Table 2
Native acrylamide amount in real food samples and % RR at from food samples spiked at two levels (5 and 50 μg kg^{-1}).

Sample	Fe_3O_4@G-TEOS-MTMOS RP-MSPE		
	Spiked level (μg kg^{-1})	Native acrylamide amount (μg kg^{-1}) ± %RSD	% Relative Recovery (% RR)
Boiled potato	0	Nd	–
	5	–	99.55 ± 1.8
	50	–	102.27 ± 2.7
Fried potato with bright-fleshed	0	900.81 ± 4.9	–
	5	–	87.31 ± 2.7
	50	–	105.97 ± 1.6
Fried sweet purple potato	0	11.38 ± 5.3	–
	5	–	91.84 ± 2.6
	50	–	99.63 ± 3.9
Fried sweet orange potato	0	21.63 ± 7.6	–
	5	–	95.44 ± 4.7
	50	–	97.58 ± 3.3
Potato chips	0	192.98 ± 4.5	–
	5	–	85.23 ± 3.2
	50	–	96.28 ± 2.4
Fried eggplant	0	133.45 ± 4.8	–
	5	–	82.70 ± 4.3
	50	–	95.19 ± 3.1
Bread (toast)	0	5.02 ± 3.5	–
	5	–	91.18 ± 2.1
	50	–	93.07 ± 1.5
Banana chips	0	18.77 ± 5.6	–
	5	–	84.89 ± 4.9
	50	–	92.96 ± 1.7
Cheese Snack	0	112.91 ± 6.8	–
	5	–	94.08 ± 6.01
	50	–	99.51 ± 3.1

cheese snack sample, after and before clean-up process, respectively. The intensity of interferences decreased after the clean-up process, and the peak area of native acrylamide (AA) also increased. In addition, the chromatograms after clean-up process (Fig. 2A and C) showed that the Fe_3O_4@G-TEOS-MTMOS is a suitable adsorbent candidate for cleaning-up process.

3.5. Chromatograms and mass ions approval

The chromatogram (scan mode) of acrylamide standard solution at 100 mg kg^{-1} is shown in Fig. 3A, while its mass ions at *m*/*z* 71 and 55 is shown in Fig. 3B. The normal EI mass spectrum of the acrylamide molecular ion $[C_3H_5NO]^+$ at *m*/*z* 71 and one ion fragment at *m*/*z* 55 show molecular ion corresponding to the loss of NH_2. Fig. 3C shows the unspiked chromatogram (scan mode) of fried potato with bright-fleshed after clean-up process using Fe_3O_4@G-TEOS-MTMOS. Fig. 3D shows mass ions of acrylamide in unspiked fried potato with bright-fleshed, where two mass peaks at *m*/*z* 71 and *m*/*z* 55 were observed. The comparison of mass analysis of unspiked sample (Fig. 3D) and standard acrylamide (Fig. 3B) indicate a sharp peak at 7.03 (stared in Fig. 3C) is as exactly as the native acrylamide in fried potato with bright-fleshed.

3.6. Comparison of current study with other published works

Table 3 shows the LODs obtained with different types of clean-up methods for various food samples such as bread, chips, potato and others. Native acrylamide found with different method was also considered. The RP-MSPE method based on Fe_3O_4@G-TEOS-MTMOS exhibited 1.5× to 850× lowest LOD (0.061 μg kg^{-1}) as compared to other methods. Also, the LLE method via derivatization gave low LOD (0.04 μg kg^{-1}), which is probably due to the tandem MS detector used. The method based on derivatization with trifluoroacetic and direct immersion single drop microextraction (DISDME) gave the highest level of acrylamide found in food samples (1781 μg kg^{-1} and 2059 μg kg^{-1}), respectively. The present Fe_3O_4@G-TEOS-MTMOS RP-MSPE method showed high level of acrylamide (900.81 μg kg^{-1}). The native acrylamide found in the

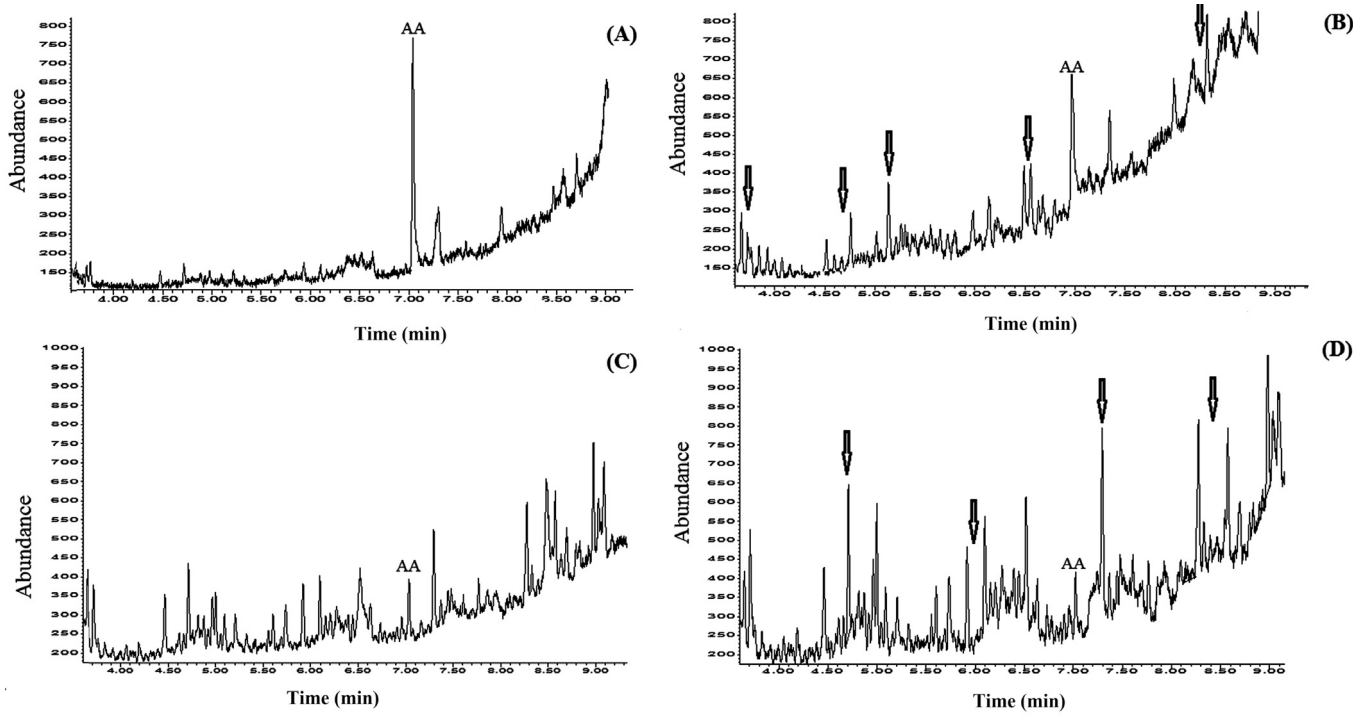

Fig. 2. Typical chromatogram (SIM mode) of acrylamide (AA) analysis from spiked and unspiked cheese snacks sample after and before cleaning using Fe_3O_4@G-TEOS-MTMOS: A) after clean-up (spiked at 5 μg kg^{-1}), (B) before clean-up (spiked at 5 μg kg^{-1}), (C) after clean-up (unspiked), and (D) before clean-up (unspiked).

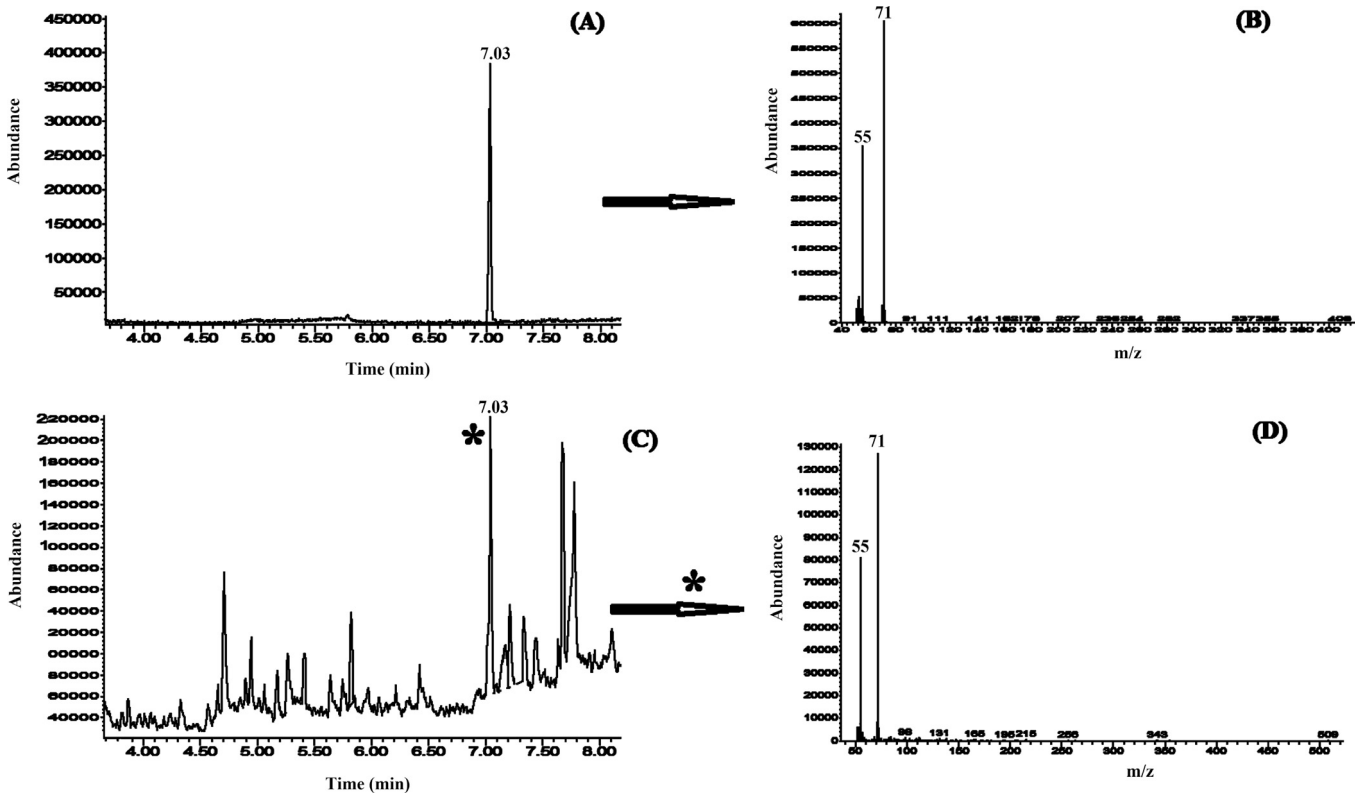

Fig. 3. Chromatogram (scan mode) for 100 mg kg^{-1} of (A) acrylamide standard solution, B) mass ions of standard acrylamide, (C) unspiked potato after clean-up process using Fe_3O_4@G-TEOS-MTMOS adsorbent, and (D) mass ions of unspiked potato.

Table 3
Amount of native acrylamide found and LOD in the present work compared to other studies.

Sample	Sample preparation method	Native found (μg kg^{-1})	LOD (μg kg^{-1})	Detector	Ref.
Boiled potato, fried potato with bright-fleshed, sweet potato, snack, banana chips, eggplant and potato chips	RP-MSPE clean-up using Fe_3O_4@G-TEOS-MTMOS	5.02–900.81	0.061–2.89	GC–MS	This current study
Fried potato with bright-fleshed, fried eggplant	d-SPE clean-up using TEOS-MTMOS	338–750	9.1–12.8	GC–MS	Omar et al. (2014)
Cookies, potato chips, fried potato with bright-fleshed and rice crust	SPE clean up using Tetraazacalixarene silica gel	13–28	5	HPLC-UV	Zhang et al. (2014)
Potato chips, biscuits, and coffee	Fluorescent sensing based on polymerization	33.9–377	3.5	LC-MS/MS	Hu et al. (2014)
Potato with bright-fleshed and corn chips	SPE clean up	120–1500	5	GC–MS	Franek et al. (2014)
Bread and potato with bright-fleshed	Enzyme Linked Immunosorbent Assay (ELISA)	168–901	0.1–5	–	Singh et al. (2014)
Twisted cruller and potato chip	MIP-SPE	218–554	72	HPLC-UV	Xu, Qiao, Ma, Zhang, and Xu (2013a)
Potato with bright-fleshed, chips (except potato chips), biscuits, French fries, breakfast cereals, chocolate products, tea, seasoned laver, and nut products	Clean-up SPE (HLB Oasis)	<1435	10	LC-MS/MS	Lee et al. (2013)
Potato chips, roasted coffee, French fries	LLE and derivatization	19.1–496	0.04	LC-MS/MS	Lim and Shin (2014)
Breakfast cereal, butter biscuit, French fries	Derivatization with trifluoroacetic	0.91–1781	1–25 2–36	GC-ECD GC-IT/MS	Russo et al. (2014)
Potato crisps	Reverse phase - drop microextraction (RP-DISDME)	1098–2059	57	GC-FID	Kaykhaii and Abdi (2013)
Binggan, Crisp Mahua, Mahua, Paicha, Yougao, Youtiao, moon cake and Cantonese moon cake	LLE	86.3–151	8.0	HPLC-UV	Wang et al. (2013)

current study is well within the range reported in previous studies (Franek et al., 2014). The excellent analytical performance of Fe_3O_4@G-TEOS-MTMOS RP-MSPE adsorbent provides powerful ability for clean-up processes.

4. Conclusion

The Fe_3O_4@G-TEOS-MTMOS RP-MSPE method was successfully applied for the clean-up and determination of acrylamide in the

various foods analysed. The fast and reliable Fe_3O_4@G-TEOS-MTMOS RP-MSPE method offers a good alternative method for clean-up of food samples for direct determination of acrylamide prior to GC–MS analysis. The current study gave superior results compared to our previous studies based on TEOS-MTMOS d-SPE and also compared to other published works. Excellent analytical performance was obtained for the Fe_3O_4@G-TEOS-MTMOS RP-MSPE method, including low LODs (0.061–2.89 μg kg^{-1}) and high relative recovery (82.70–105.97%). Under the optimum conditions, the proposed Fe_3O_4@G-TEOS-MTMOS RP-MSPE method successfully determined native acrylamide based on two ions at *m*/*z* 71 and *m*/*z* 55 in various food samples; the highest acrylamide was in fried potato with bright-fleshed (900.81 μg kg^{-1}) and the lowest acrylamide was in toasted bread (5.02 μg kg^{-1}).

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