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Determination and extraction of acrylamide in processed food samples using alkanol-based supramolecular solvent-assisted dispersive liquid-liquid microextraction coupled with spectrophotometer: Optimization using factorial design

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ABSTRACT

In current study, simple, rapid, sensitive and selective alkanol-based supramolecular solvent-assisted dispersive liquid-liquid microextraction (SSA-DLLME) method was first time developed for the extraction and determination of acrylamide (AA) in coffee, chocolate, roasted nuts, French fries, cereals, biscuits, chips, bread and caramelized fruit using UV–visible spectrophotometer. Different parameters were investigated and optimized to know their effects on the extraction of AA. Studies have shown that effective extraction of AA was achieved at short vortex time (2 min) and acidic pHs. Extraction of AA was inversely proportional to sample volume. The linear range (LR) of the SSA-DLLME method was 0.6–350 ng mL^{-1}. The limit of detection (LOD), and limit of quantification (LOQ) were found to be 0.2 ng mL^{-1} and 0.6 ng mL^{-1}, respectively. In addition, enhancement factor and preconcentration factor was 114 and 200, respectively. Factorial design was utilized to better understand dual effluents of factors on extraction recovery of the AA. Optimized SSA-DLLME method was successfully applied to process food samples for the determination of AA.

1. Introduction

Acrylamide (AA) is a very reactive and compound belong to amides. The chief source of AA in human are foodstuffs based on many foods mostly coffee, cereals and potatoes when frying, roasting foods at temperature higher than 120 °C (Raffan and Halford, 2019). The AA level may vary significantly in same food using different thermal handling conditions. For instance, high contents of carbohydrate foods such as potatoes and cereals treated at higher than 120 °C temperature comprise very higher levels of AA (Franek et al., 2014). The large level of animal investigates indicated that AA possesses generative toxicity, severe neurotoxicity and genotoxicity (Karimani et al., 2021; Larguinho et al., 2014). The AA has involved significant attention to food safety because of its negative impacts on human. International Agency for Research on Cancer (IARC) has considered AA as a doubted chemical poison for humans (Hu et al., 2015). The Commission Regulation (EU) has set a standard level of AA in food at 400–4000 μg kg^{-1} (Zhuang et al., 2022). Recently, the European Union (EU) has recommended the limits of maximum residue (MRLs) of AA in foodstuffs including breakfast cereals, baby food, soft bread and roast coffee to be 300–850 μg kg^{-1} (EU, 2017). Therefore, there is a necessary for the development of an inexpensive and fast method for measurement of AA in food samples (Nayak et al., 2017; Yan et al., 2022).

AA is produced in food because of the Maillard reaction (MR) among amino acids mostly (asparagine) and sugar (fructose and glucose) (Onacik-Gür et al., 2022). The Maillard reaction corresponds to several non-enzymatic reactions among the compound and reducing sugars with a free amino group (Monsalve-Atencio et al., 2022). The MR reaction is

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further distributed into 3 stages, initial, middle and also final step. In the initial stage amino groups and reducing sugars condensation is takes place through Schiff's base creation, main creation of N-glycosylamine through Amadori reorganisation (Nursten, 2005). The intermediate stage, start from the product of the initial stage (Amadori) and contains the fragmentation and dehydration of sugar and decomposition of amino acids and also liberating of the amino group (Nursten, 2005). In final stage, previously generated product of intermediate reacts with each other through polymerization and creating brown heterocyclic nitrogen (N) compounds (melanoidins) and have molecular weight > 100,000 g mol^{-1}) (Nursten, 2005). Polymerization dehydration and fragmentation reaction take place at this step (Van Boekel, 2006; Monsalve-Atencio et al., 2022). There are many research work reported for examining of AA and used different methods. Altunay et al., 2018 determined and extraction of AA from thermally treated foods via IL-UASME by spectrophotometry. LOQ and LR were found 2.3 μg kg^{-1} and 2.3–350 μg kg^{-1}. Altunay et al., 2016 used the preconcentration process for indirect analysis of AA from cereal foods, crackers and chips by FAAS. LOQ and LR were found 0.28 μg kg^{-1} and 0.3–150 μg kg^{-1}. Nematollahi et al., 2020 determined AA in 24 different kinds of roasted seeds and nuts by microextraction process by GC-MS. LOQ and LR were found 2 μg kg^{-1}, 5–500 μg kg^{-1}. Reported LOQ and LR values were found agreement with MRLs. Schettino et al., 2020 determined the AA in cosmetic products by DLLME using liquid chromatography. Desmarchelier et al., 2022 determined the AA from food samples using LC-MS/MS method. Oellig et al., 2022 assessed the AA in vegetable chips through liquid chromatography–mass spectrometry. Ghiasvand and Hajipour, 2016 reported direct analysis of AA in potato chips used headspace SPME coupled by GC. Yamini et al., 2012 analyzed the trace level of AA impurity in water using DLLME by GC. Russo et al., 2014 analyzed the AA in potato chips conservative cereal-based foods by a change to 3-[bis (trifluoroethanoyl) amino]− 3-oxopropyl trifluoroacetate using GC. Kaykhaii and Abdi., 2013 assessed the AA in potato crisps by gas chromatography using reversed-phase direct immersion single drop microextraction method. The alkanol-based supramolecular solvent (SUPRAS) has distinctive physicochemical possessions and making it very important to substitute organic solvents in the extractions. The SUPRAS has the ability to dissolve solutes with an extensive polarity, compartmentalize, organic, concentrate and attain high extraction efficiencies, mostly because of mixed-mode structures and provided various binding sites (Peyrovi et al., 2017). Therefore, alkanol-based supramolecular solvent (SUPRAS) has been successfully applied to organic compounds (Ballesteros-Gómez et al., 2010), extractions of metals (Ojeda and Rojas, 2009) and food, environmental and biological analytes (Rezaei et al., 2015; Rezaei et al., 2013; Moradi and Yamini., 2012).

In current the study, simple, rapid, sensitive, selective and green alkanol-based supramolecular solvent-assisted dispersive liquid-liquid microextraction (SSA-DLLME) method was first time developed for the extraction and determination of acrylamide (AA) in processed food samples including coffee, chocolate, roasted nuts, French fries, cereals, biscuits, chips, bread and caramelized fruit using a UV–visible spectrophotometer. Factorial design was utilized to observe the dual impacts of variables on the extraction.

2. Experimental

2.1. Chemicals and reagents

All chemicals were utilized in microextraction and used directly with no further purification. The AA was bought from Sigma company (Sigma-Aldrich, St. Louis, MO, USA), and prepared 1000 mg L^{-1} stock solution by proper dilution in methanol. Calibration solutions (0.1, 0.5, 1, 5, 10, 25, 50, 100, 250 and 500 ng mL^{-1}) were ready by further dilution of solution in methanol and before analysis it was stored at 4 °C. For the preparation of alcohol-based supramolecular solvents, undecanol (≥ 97.5% (a/a)), heptanol (≥ 99.0% (a/a)), tetrahydrofuran (≥ 99.5%), sodium dodecyl sulfate (≥ 85.0%, SDS) and tetrabutylammonium bromide (≥ 99.0%, TBABr) were bought from Merck (Darmstadt, Germany). Anhydrous $MgSO_4$ (Sigma), n-hexane (≥ 96.0%, Sigma), acetonitrile (Merck), and primary secondary amine (PSA, Merck) were utilized in the pre-preparation of processed food samples. Adjusted pH of the solutions using buffer solutions like borate, phosphate, acetate and phthalate.

2.2. Apparatus

The analysis step was achieved with a dual-beam spectrophotometer (UV-1800, Shimadzu, Japan) connected to a personal computer equipped with 10 cm quartz cells microcuvette (500 μL) and loaded with UV-Probe 2.42 software. The dispersive step in the developed microextraction approach was achieved by using vortex (VG3 model, IKA, Germany). Centrifuge (Universal-320, Hettich, London, England) and ultrasonic bath (SK5210LHC Kudos, Shanghai, China) were utilized for sample handling and pH sample was checked via pH meter (Selecta 2001 Sartorius, North America).

2.3. Preparation of alkanol-based supramolecular solvents

In the current study, prepared three different alcohol-based supramolecular solvents for rapid extraction of AA from processed food samples. Before the reported method was utilized for preparation of solvents. The data about the prepared supramolecular solvents were presented in Table S1.

2.4. Collection and pre-treatment of processed food samples

The samples extracted and analyzed in this study were bought from markets in Sivas, Turkey. Coffee, chocolate, roasted nuts, French fries, chips, cereals, biscuits, bread and caramelized fruit/vegetable products were selected as processed samples. In addition to these, two certified reference materials (ERM-BD274-rusk and ERM-BD272-crisp bread) were used for the validation test of the developed method. The method previously reported by our study group was used to turn the selected samples into solution before applying the developed method (ALOthman et al., 2020; Seebunrueng et al., 2020; Altunay et al., 2018; Altunay et al., 2016).

2.5. Developed microextraction approach

Developed microextraction approach was carried out in 15 mL centrifuge tubes. First, 1.0 mL of food sample (in Section 2.4) was transferred to the centrifuge tubes, followed by pH adjustment of the sample solutions to pH= 5.5. Then 400 μL of the prepared SUPRAS-2 (SDS/ TBABr/ $AlCl_3$) was injected into solution by syringe. Immediately after this step, tube was vortexed for 2 min at 1500 rpm to increase dispersibility. After standing for about 3 min at room temperature, two separate phases were formed. Aqueous phase was taken with a syringe and waste. The final volume of the sample was made up to 500 μL by methanol and spectrophotometric absorbance was measured at 298 nm. All runs described above were replicated in the sample blank. The UV spectrum obtained for three different AA concentrations in 1.0 mL of the sample solution under optimum conditions was given in Fig. S1. In addition, the calibration curve obtained from the model solutions of AA was presented in Fig. S2.

2.6. Experimental design

The factorial design (two-level) was drawn to check the impacts of independent variables on recovery of the AA using CCD method and low (−1) and high (+1) level of variables were used to draw the design (Viegas et al., 2021). Four variables including vortex time, pH, sample volume and solvent volume were applied in the factorial design (see

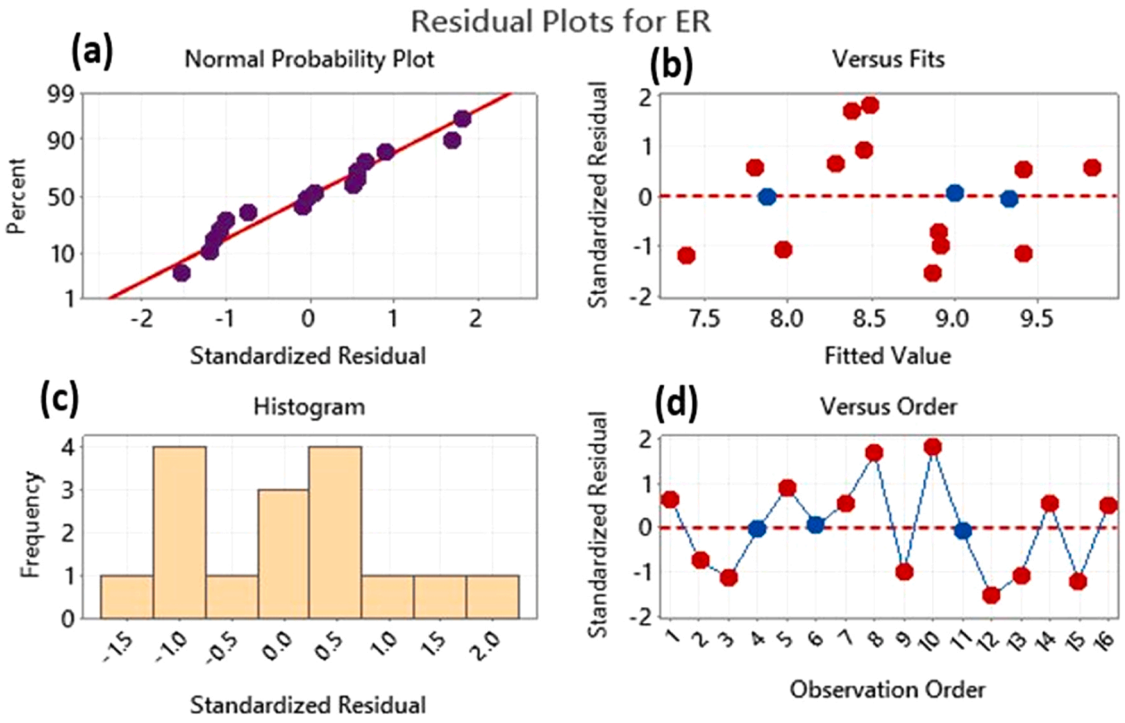

Fig. 1. Residual plots of effects (a-d).

Table S2). A total of 16 experiments were run with low and high values of the variables (see Table S3).

3. Results and discussion

3.1. Factorial design using (central composite design) method

The factorial design was drawn to know the dual impacts of applied variables on extraction of AA and also showed significant and insignificant effects of variables. The effects of parameters on the recovery of acrylamide and interaction of parameters were examined by factorial design using central composite design (CCD) method with the help of Minitab software. The interaction of combined variables was estimated by drawn the factorial design such as Pareto chart, residual plots, response surface plots, ANOVA. The plots are very capable to know the simultaneously combined impacts of factors on the recovery of acrylamide.

3.1.1. Pareto chart

Pareto chart was drawn to know the standardized effluents of main parameters on recovery of AA. The standardized effect may be imagined with at 95% confidence interval with an alpha value of 0.05 (see Fig. S3). The critical value of the baseline was obtained as 8.35. It states that the experimental value of these variables is higher than the critical

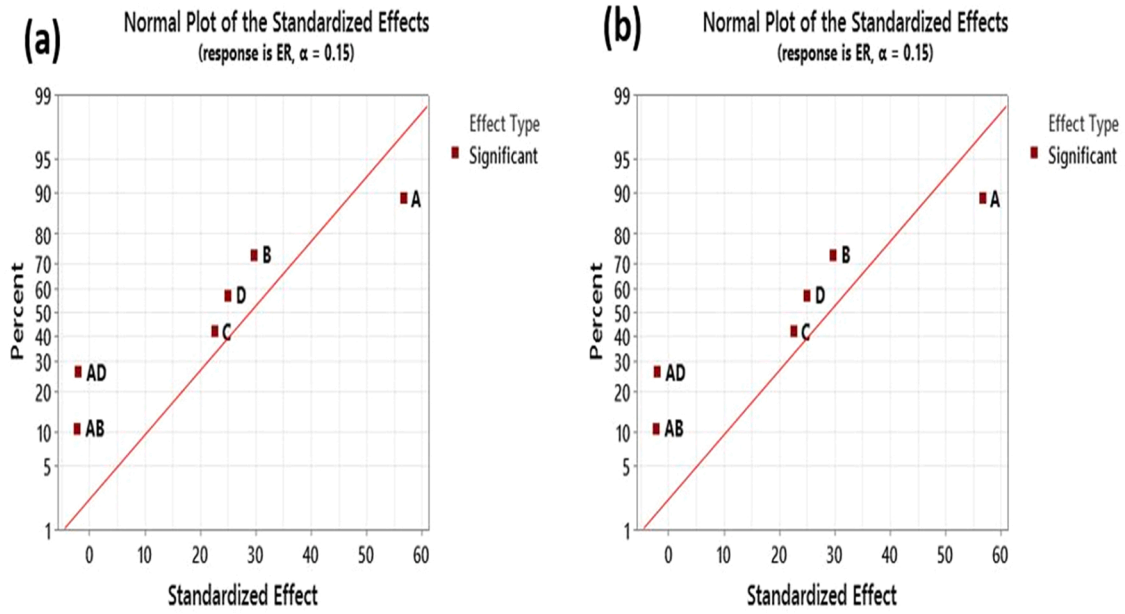

Fig. 2. Normal probability (a) and half normal probability plot (b).

value and shows significant effects (Ali et al., 2021). The pareto chart of variables such as A (pH), B (SUPRAS-2), C (vortex time) and D (samples volume) overlapped the line and showed significant impacts but variable AB and AD were not crossed the line and considered insignificant effects.

3.1.2. Surface response chart

The surface response plot was drawn to predict the response of variables to the extraction recovery of the AA (see Fig. S4). Although surface response plots were drawn for 2 factors based on the optimal values (Yıldırım and Sellitepe, 2021; Altunay et al., 2021). The surface plot (Fig. S4a) described pH versus SUPRAS-2 solvent and results from expression that acidic pH was favorable for attaining greater recovery and a good response was attained at pH= 5.5. Also, SUPRAS-2 solvent volume 400 μL was favorable for better recovery. The surface plot (Fig. S4b) described pH versus vortex time and results showed that low vortex time 2 was favorable for reaching better recovery. Higher response was attained at vortex time 2 min. Surface plot (see Fig. S5a) described pH versus volume of samples. Results presented that low volume of samples showed good recovery, when volume of sample was increase the recovery was decreased. Highest recovery was found when the sample volume was 10 mL. Surface plot (see Fig. S5b) defined SUPRAS-2 solvent versus vortex time. The results indicated that 400 μL of SUPRAS-2 solvent and vortex time 2 min was shown better extraction recovery for AA. The surface plot (Fig. S6a) described SUPRAS-2 solvent versus sample volume. The obtained results showed that better recovery was found at low sample volume and recovery of AA was inversely proportional to sample volume. The surface plot (see Fig. S6b) described vortex time versus volume of sample. Obtained results exhibited that better recovery was achieve at low vortex time 2 min and a low volume of sample.

3.1.3. Residual effects

The residual effects plots showed the significant and insignificant impacts of the variables on recovery of the AA (see Fig. 1a). The residual plot (see Fig. 1a) showed that the most of the dots along with the reference line indicated no significant effects of variables. The plot (Fig. 1b) described that most of points drops away from line that indicated significant impact on the extraction recovery. The histogram plot (Fig. 1c) described that bar line were distributed in negative and positive value and showed the significant and insignificant impacts of variables in the extraction recovery of the AA. The residual plot (Fig. 1d) defined that points drops away from line and indicated significant level of model.

3.1.4. Normal probability and half normal probability plots

Normal probability (see Fig. 2a) and half normal probability plots (see Fig. 2b) defined the variable such as A (pH), B (SUPRAS-2) solvent, C (vortex time), D (sample volume), AB and AD showed significant effects. All points fall away from line and indicated significant impacts on the extraction recovery of the AA.

3.1.5. ANOVA analysis

The significant and adequacy of the independent models were assessed via ANOVA. The variable showed with p-value (<0.05) considered as a significant effect on response (see Table S4). If the variable which is p-value (> 0.05) indicated not significant or lack of fit (Viegas et al., 2021). The ANOVA showed that AB and AD had p values greater than 0.05. Therefore, these interactions are insignificant effects.

3.2. Optimization of parameters

The study is focused on the analysis of AA in different foods and vegetable samples by newly developed method alkanol-based supramolecular solvent-assisted DLLME by UV-Visible spectrophotometer. Effect of pH was observed by altering pH from 2.5 to 9.5. The pH level was adjusted by using the buffer solutions prepared in Section 2.1. The results indicated that best analytical signal was found at pH 5.5 (see Fig. S7). The results confirmed that recovery of AA was low at acidic pH, it may be due to the protonation. Hence, pH 5.5 was considered optimum for further experimental work. In the current study, three different types of supramolecular solvents (SUPRAS-1 SUPRAS-2 and SUPRAS-3) with different polarity and chemical properties used to determine the AA from food samples. The SUPRAS-2 showed best absorbance signal and recovery of AA as compared to SUPRAS-1 and SUPRAS-3 (see Fig. S8). The different volume of SUPRAS-2 was used for the extraction of AA in the range of 100 and 700 μL. The 400 μL volume of SUPRAS-2 indicated maximum recovery of AA and minimum recovery was found at 100 μL volume of SUPRAS-2 (see Fig. S9). Therefore, optimized 400 μL SUPRAS-2 vol for further work. The vortex time ranged from 0.5 to 4 min was applied and check their effects on the recovery of AA. The vortex procedure is very effective in increasing the sample allocation from liquid phase to the surfactant phase for extraction of the AA (see Fig. S10). The vortex time 2 min showed maximum recovery of AA and 0.5 min showed minimum recovery. Therefore, 2 min vortex time was optimized for further experimental time. The five types of diluent agents acetonitrile, MeOH, EtOH, THF and heptanol were used and check their effects on the extraction recovery of the AA in food samples (see Fig. S11). The diluent agents MeOH showed maximum extraction recovery of AA as compared to other diluent agents. Therefore, MeOH diluent agent was optimized for further experimental work. The volume of the sample is significant in the microextraction process. The different volume 10, 20, 50, 75, 100, 125, 150 and 200 mL of sample was taken and utilized for determination of AA (see Fig. S12). The findings showed maximum recovery of AA was obtained at 10 mL sample volume. These parameters are capable to effect on the recovery of acrylamide and these factors interact to each other.

Table 1
Summary of calibration parameters obtained using the developed microextraction approach.

Parameters	Developed microextraction approach
Linear equation	A= 0.0219[acrylamide] + 0.0095
R^2	0.9972
Linear range (ng mL^{-1})	0.6–350
LOD (3 s/m) (ng mL^{-1})	0.2
LOQ (10 s/m) (ng mL^{-1})	0.6
EF	114
PF	200
*Matrix effect (%)	4–12

s: standard deviation of 10 replication analysis of blank samples, m: slope of calibration graph
* Matrix effect %= ((slope of matrix-matched calibration curves /slope of standard calibration curves)− 1)× 100
If Matrix effect % is $\leq +20\%$ and $\geq -20\%$, then no matrix effect is present; values $> +20\%$ and $< -20\%$ indicate signal microextraction and suppression, respectively (Szarka et al., 2022).

3.3. Method performing conditions

The method was validated by performing different analytical working conditions including linearity equation, correlation coefficient, LOD (3 s/m), enhancement factor (EF), LOQ (10 s/m), preconcentration factor (PF), RSD and matrix effects were optimized (see Table 1). The linearity equation was taken A= 0.0219 (AA) + 0.0095 with R^2 value was 0.997 and linearity 0.6–350 ng mL^{-1} applied for analysis of AA. The value of LOD was 0.2 ng mL^{-1} and LOQ was 0.6 ng mL^{-1}. The EF (114) was calculated from the slope of the calibration graphs obtained before and after the microextraction step. The PF (200) was calculated as the ratio of the sample volume to the final volume. The different matrix ions were applied to the samples and checked their effects on the extraction recovery of the AA and no particular effects of matrix effects were

Table 2
The effect of foreign ions on recovery of 100 ng mL^{-1} of acrylamide (N = 3).

Ion	*Tolerable limit	Recovery (Mean ± standard deviations)
K^+	10000	98.2 ± 2.4
SO_4^{2-}	10000	98.7 ± 2.4
Acetaldehyde	5000	98.5 ± 1.9
Mg^{2+}	5000	98.1 ± 2.7
Na^+	5000	97.6 ± 2.0
Acetate	5000	98.8 ± 3.2
Al^{3+}	1000	98.3 ± 3.7
Co^{2+}	1000	98.0 ± 2.9
2-Nitrobenzaldehyde	1000	97.4 ± 2.7
Fe^{3+}	750	97.6 ± 3.1
Ag^+	750	97.7 ± 2.8
2-Chlorobenzaldehyde	500	96.3 ± 3.0
Hydrazine	500	96.5 ± 2.6
Bromobenzaldehyde	250	96.0 ± 3.9
Zn^{2+}	250	95.4 ± 3.7

* [Foreign ions amount]/ [acrylamide amount]

Table 3
Results of intraday and interday studies for the developed microextraction approach.

Added (ng mL^{-1})	Intra-day studies (N = 3)			Inter-day studies (N = 3 ×3)		
	Found (ng mL^{-1})	RSD (%)	Recovery (%)	Found (ng mL^{-1})	RSD (%)	Recovery (%)
5	4.8	1.9	96.0	4.6	2.7	92.0
100	98.4	2.5	98.4	96.5	4.0	96.5
300	297.6	3.7	99.2	293.4	4.6	97.8

Table 4
Determination of acrylamide in certified reference materials (N = 5).

Reference materials	Validation parameters	Experimental data
ERM-BD272 (crisp bread)	Certified value (mg kg^{-1})	0.98 ± 0.09
	Found value (mg kg^{-1})	0.96 ± 0.03
	Recovery (%)	98.0
	*$t_{exp.}$	1.49
ERM-BD274 (rusk)	Certified value (μg kg^{-1})	74.0 ± 7.0
	Found value (μg kg^{-1})	73.1 ± 2.8
	Recovery (%)	98.8
	*$t_{exp.}$	0.72

observed.

3.4. Effects of foreign ions on the extraction recovery of acrylamide

In extraction studies, investigating the effect of possible foreign ions has a key role to evaluate the matrix effect of the method. When determine the real samples, the effects of foreign substances were observed. Therefore, selectivity of the proposed method must be evaluated. The finding showed that 1–5% effects of the foreign matrix were observed on the extraction recovery of the AA (see Table 2). Recovery values were found quantitative at high tolerance limits. As a finding, we can say that the developed method is capable to the determination of the AA and no particular effect was observed on the extraction recovery of the AA.

3.5. Inter-day and intra-days studies

The inter- and intra-day precisions were studied to know the effects of time in the extraction recovery of the AA. The samples were prepared in triplicate at each concentration 5, 100 and 300 ng mL^{-1} were added for experimental replicates. The intra-day study was obtained 4.8, 98.4 and 297.6 ng mL^{-1} for added values of 5, 100 and 300 ng mL^{-1} with recovery was 96.0%, 98.4% and 99.2%, respectively. The inter-day study results were obtained 4.6, 96.5 and 293.4 ng mL^{-1} for added values of 5, 100 and 300 ng mL^{-1} with recovery was 92.0%, 96.4% and 97.2%, respectively and good RSD% value 1.9–4.6% were observed (see Table 3). The finding revealed that recovery of inter-days was decreased as compared to intra-day study, it may be due to the interference of ions.

Table 5
Recovery obtained from the determination of acrylamide in processed food samples (N = 3).

Samples	Added (μg kg^{-1})	Found (μg kg^{-1})	RSD (%)	Recovery (%)
Coffee	–	1.4	1.5	–
	10	11.1	1.8	97.0
	50	50.8	2.9	98.8
Chocolate	–	n.d*	–	–
	10	9.5	1.9	95.0
	50	48.7	2.7	97.4
Roasted nuts	–	2.8	1.2	–
	10	12.1	2.5	93.0
	50	50.7	3.2	95.8
French fries	–	2.1	2.0	–
	10	11.7	2.4	96.0
	50	51.0	2.9	97.8
Chips	–	4.9	2.6	–
	10	12.4	3.3	95.0
	50	53.8	3.7	97.7
Cereals	–	n.d	–	–
	10	9.6	1.8	96.0
	50	49.2	2.4	98.4
Biscuits	–	n.d	–	–
	10	9.7	1.3	97.0
	50	49.1	1.7	98.2
Breads	–	1.1	1.0	–
	10	10.4	1.6	93.0
	50	50.0	2.2	97.8
Caramelized vegetable	–	n.d	–	–
	10	9.8	1.7	98.0
	50	49.6	2.9	99.2
Caramelized fruit	–	n.d	–	–
	10	9.4	2.1	94.0
	50	48.3	3.4	96.6
Turkish coffee	–	7.2	2.0	–
	10	16.8	2.3	96.0
	50	55.8	2.5	97.2
Roasted Coffee	–	14.9	2.4	–
	10	24.6	2.7	97.0
	50	64.2	2.9	98.6
Rusks	–	n.d	–	–
	10	9.5	1.8	95.0
	50	48.4	2.1	96.8
Kemalpasa dessert	–	22.8	1.7	–
	10	32.4	2.0	96.0
	50	71.6	2.4	97.6

* could not be determined

Table 6
Comparison the determination of acrylamide with reported methods.

Instruments	Method	LOD [a]	LOQ [b]	LR [c]	ER [d]. (time min)	PF [e]	EF [f]	RSD% [g]	References
HPLC	SLE	0.03 μg mL^{-1}	0.10 μg mL^{-1}	0.05–10 μg mL^{-1}				8	González-Gómez et al., 2021
GC–MS	DLLME	0.6 μg kg^{-1}	2 μg kg^{-1}	5–500 μg kg^{-1}	10	116		8.9	Nematollahi et al., 2020
UPLC-MS/MS	DLLME	3 μg L^{-1}	10 μg L^{-1}	3.0 – 100.0 μg L^{-1}	1.0	0.8		1.1	Galuch et al., 2019
GC-ECD	SDME	0.6 μg L^{-1}	2 μg L^{-1}	2.0–100.0 μg L^{-1}	15				Saraji and Javadian, 2019.
GC-MS	DLLME	0.6 ng g^{-1}	2 ng g^{-1}	1–500 ng g^{-1}.	10.25	116		5.45	Nematollahi et al., 2019
Spectrophotometer	IL-UAME	0.7 μg kg^{-1}	2.3 μg kg^{-1}	2.3–350 μg kg^{-1}	10	120/95		2.2	Altunay et al., 2018
FAAS	UA-CPE	0.08 μg kg^{-1}	0.28 μg kg^{-1}	0.3–150 μg kg^{-1}	2.5	93.5		6.30	Altunay et al., 2016
GC-MS	SPME	10 μg kg^{-1}	10 μg^{-1}		15			10.9	Cagliero et al., 2016
HPLC	SPDE	1.5 μg kg^{-1}		10–300 μg kg^{-1}	20		4.3		Zhao et al., 2015
GC-MS	DSPE	9.1–12.9 μg kg^{-1}	27.8–38.9 μg kg^{-1}	50–1000 μg kg^{-1}	1–6		6.6		Omar et al., 2014
HPLC	MIPSPE	72 ng^{-1}		0.5–500 μg^{-1}	20	93	4.7		Xu et al., 2013
Spectrophotometer	SSA-DLLME	0.2 ng mL^{-1}	0.6 ng mL^{-1}	0.6–350 ng mL^{-1}	2	200/114	8		Present work

Ionic liquid-based ultrasound-assisted selective microextraction (IL-UAME), Supramolecular solvent-assisted dispersive liquid-liquid microextraction (SSA-DLLME), Flame atomic absorption spectrometry (FAAS), Ultrasonic-assisted cloud point extraction (UA-CPE), Solid-phase microextraction (SPME), Dispersive solid-phase extraction (DSPE), Gas chromatography–mass spectrometry (GC-MS), Molecularly Imprinted Polymer Solid-Phase Extraction (MIPSPE), Solid-liquid extraction (SLE), Gas chromatography-electron capture detection (GC-ECD), Single-drop microextraction (SDME), Ultra-performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS), (a) Limit of detection (LOD) (μg/kg), (b) Limit of quantification (LOQ) (μg/kg), (c) Linear range (LR) (μg/kg), (d) Extraction recovery time (ER), (e) Pre-concentration factor (PF), (f) Enrichment factor (EF), (g) Relative standard deviation (RSD)

3.6. Determination of acrylamide in certified reference materials (N = 5)

The accuracy of developed method was optimized by analysing of certified reference constituents. The extraction recovery of AA in certified reference materials ERM-BD272 (crisp bread) and ERM-BD274 (rusk) were observed (see Table 4). The recovery of certified reference materials ERM-BD272 (crisp bread) and ERM-BD274 (rusk) were found 98.0% and 98.8%, respectively.

3.7. The recovery of acrylamide in processed food samples

The recovery of AA in different food samples such as coffee, chocolate, roasted nuts, chips, cereals, biscuits, French fries, bread, caramelized vegetables and caramelized fruits were observed at three different concentrations of AA as 0, 10 and 50 μg g^{-1} was added in the sample. The findings showed 93–99.2% recovery of AA was obtained (see Table 5). The maximum recovery of AA was obtained in caramelized vegetable samples as 98% and 99.2% and the minimum result was obtained in roasted nuts samples as 93% and 95.8%. The results confirmed that the developed method showed good recovery of AA.

4. Conclusions

A new and simple alkanol-based (SSA-DLLME) method was developed for investigation of AA in different food samples by using a spectrophotometer. SSA-DLLME has some advantages such as highly rapid, sensitive, efficient, and selective. Present study can be comparable with power techniques like UPLC-MS/MS, HPLC and GC-MS in Table 6. The extraction of AA was higher at acidic pH 5.5, SUPRAS-2 and vortex time 2 min. It was observed that when volume of the sample was increased, extraction of AA was decreased. The linearity range 0.6–350 ng mL^{-1} applied for extraction of AA with LOD value was 0.2 ng mL^{-1}. In addition, LOQ, EF and PF were 0.6 ng mL^{-1}, 114 and 200, respectively. Reported LOQ and LR values were found agreement with MRLs. The factorial design method was applied to better understand the dual impacts of variables on the extraction recovery of the AA and significant and insignificant characteristics of the variables. The foreign ions did not show impacts on the method was found high. So, present SSA-DLLME method may be utilized for the recovery of complex food samples.

Ethics approval and consent to participate

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Consent for publication

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CRediT authorship contribution statement

Nail Altunay: Investigation, Validation, Writing – original draft, Writing – review & editing, Software. **Adil Elik:** Investigation, Supervision. **Mustafa Tuzen:** Investigation, Validation, Writing – original draft, Writing – review & editing, Software. **Muhammad Farooque Lanjwani:** Investigation, Writing – original draft, Writing – review & editing, Software. **Mohammad Reza Afshar Mogaddam:** Writing – original draft, Writing – review & editing, Software.

Data Availability

The data that has been used is confidential.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2022.105023.

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