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روش میکرواستخراج فاز مایع با فیبر توخالی برای تعیین سه علف‌کش تری‌آزین در نوشابه‌های تخمیری محلی اتیوپی

سولمن سایم[۱]، نیگسی مگرسا[۱]، آبرا گرو[۱،۲*]
۱. گروه شیمی، دانشگاه آدیس آبابا، آدیس آبابا، اتیوپی
۲. گروه شیمی، دانشکده علوم طبیعی، دانشگاه جیمما، جیمما، اتیوپی
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Hollow Fiber Based Liquid Phase Microextraction Method for the Determination of Three Triazine Herbicides from Locally Brewed Ethiopian Beverages

Solomon Sime[1], Negussie Megersa[1], Abera Gure[1, 2*]
1. Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia
2. Department of Chemistry, College of Natural Sciences, Jimma University, P.O. Box 378, Jimma, Ethiopia
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چکیده
در این مطالعه روش میکرواستخراج فاز مایع با فیبر توخالی برای استخراج انتخابی و پیش تغلیظ علف‌کش‌های تری‌آزین (آتراتون، دسمترین و آترازین) از نوشابه‌های تخمیری محلی اتیوپی قبل از جداسازی و تعیین کمی توسط کروماتوگرافی مایع با کارآیی بالا با آشکارساز آرایه دیودی توسعه و گزارش گردید: پارامترهای مؤثر بر بازدهی استخراج شامل نوع حلال استخراج کننده، حجم و pH محلول نمونه، سرعت هم خوردن، زمان استخراج و غلظت نمک بررسی و شرایط بهینه تعیین گردید. تحت شرایط بهینه، حدود تشخیص و تعیین به ترتیب در محدوده‌های ۰,۰۴-۰,۰۲ و ۰,۱۲-۰,۰۵ میکروگرم بر لیتر بودند. منحنی-های کالیبراسیون در رنج ۲- ۰,۱ میکروگرم بر لیتر با ضرایب همبستگی ۰,۹۹۰ یا بهتر بودند. دقت مطالعات روزانه که به صورت انحراف استاندارد نسبی بیان می‌شود زیر ۸ درصد بود. بازیابی‌های نسبی رضایت‌بخشی برای آنالیت‌های مورد نظر بجز آترازین در نوشابه‌های نچ‌تلا و فیلترتلا بدست آمد. نتایج این تحقیق نشان می‌دهد که روش پیشنهادی، یک روش مؤثر برای استخراج و پیش تغلیظ انتخابی باقیمانده‌های علف‌کش‌های مورد نظر در نوشابه‌های تخمیری محلی اتیوپی همانند ماتریس‌های مشابه با نمونه می‌باشد.

واژه‌های کلیدی
فیبر توخالی؛ میکرواستخراج فاز مایع؛ نوشابه‌های اتیوپی؛ علف‌کش‌های تری‌آزین.

Abstract
In this study, hollow-fiber based liquid-phase microextraction method was developed of for selective extraction and/or preconcentration of triazine herbicides (atratone, desmetryn and atrazine) from locally brewed Ethiopian beverages prior to their separation and quantitative determination by high performance liquid chromatography with diode array detector. Parameters influencing extraction efficiency of the method including types of the extraction solvent, volume and pH of the sample solution, shaking speed, extraction time and salt concentration were investigated and optimum conditions were established. Under the optimal conditions limits of detections and quantifications were ranged from 0.02–0.04 and 0.05–0.12 µg/L, respectively. Calibration curves were linear over the range of 0.1–2 µg/L with coefficient of determinations of 0.990 or better. Intra- and inter-day precision studies, which were expressed as relative standard deviations were below 8 %. Satisfactory relative recoveries were also obtained for the target analytes, except for atrazine in Nech Tela and Filter Tela, which exhibited relatively lower recoveries. The results of the study indicated that the proposed method is an efficient alternative for selective extraction and/or preconcentration of residues of the target pesticides form Ethiopian locally brewed beverages as well as other similar sample matrices.

Keywords
Hollow-Fiber; Liquid Phase Microextraction; Ethiopian Beverages; Triazine Herbicides.

*Corresponding Author: aberagure@gmail.com and abera.gure@ju.edu.et

1. INTRODUCTION

Triazine herbicides are extensively used as selective pre- and post-emergence herbicides for the control broadleaf and grassy weeds in agricultural crops such as corn, wheat, barley, sorghum, grape, peaches, apple, soybeans and sugarcane. They are also used for non-agricultural purposes like soil sterilization and road maintenance [1-5].

Triazine herbicides and some of their metabolites are considered as chemical pollutants because of their potential toxicity and persistent in water, soil, sediment and biological organisms [6]. They are categorized as human carcinogen [5]. As a result, several legislative authorities have set their maximum residue level (MRL) in waters and various types of foods [7-10]. Therefore, it is important to develop rapid, simple, selective and sensitive sample preparation method for the regular monitoring of trace level residues of triazine herbicides in various matrices that are usually utilized for human consumptions.

Analysis of residues of triazine herbicides from the complex matrices usually requires sample preparation step, which plays important role for selective extraction and/or preconcentration of the target analytes prior to their instrumental determination [11-13]. In the last couple of decades, several simple, rapid and attractive alternative sample preparation methods have been proposed to replace the traditional methods: liquid-liquid extraction, LLE [11, 12] and solid phase extraction, SPE [14]. These traditional methods have several drawbacks including longer extraction time, labor intensiveness and the requirement of large quantities toxic organic solvents. Among several proposed methods, liquid-phase microextractions (LPME), in various modalities, have taken the leading rank for the extraction as well as preconcentration of s-traizine herbicides from aqueous and other matrices. For instance, solidification of a floating drop for liquid-phase microextraction, SFD-LMPE [6]; single drop microextraction, SDME [15]; dispersive liquid–liquid microextraction (DLLME) [5, 16]; solvent-terminated DLLME [17]; hollow fiber-protected liquid-phase microextraction (HF-LPME) [3, 18, 19]; and liquid–liquid–solid microextraction (LLSME) [20] were proposed for extraction and preconcentration of s-triazine herbicides from environmental water samples.

LPME methods are generally, characterized by possessing advantages such as simplicity, lower cost, negligible consumption of organic solvents and high enrichment efficiency [21]. The trends, classification, operational principles and applications of various LLME techniques have been reviewed [22-24]. In this paper, a three-phase HF-LPME in combination with high performance liquid chromatography with diode array detector (HPLC-DAD) has been proposed for the determination of the residues of three traizine herbicides, namely, atrazine, desmetryn and atratone from locally brewed Ethiopian beverages. In Ethiopia, triazine herbicides have been utilized in the agricultural farmlands, since early of 1970s [25].

Locally brewed (fermented) Ethiopian beverages might be considered as home-brewed beer which differs from commercial beers in many ways. They are produced relatively in a small scale and usually utilized for local consumption, in both rural and urban communities during occasions such as marriage ceremonies, annual festivals and social gatherings, settling disputes, and so on [26]. The very popular Ethiopian fermented beverages include tella, filter, tej, araki, korefe, shamita, keribo and borde. Among these tella, araki, filter and Tej are alcoholic, whereas the remaining are considered as low or non-alcoholic beverages [26-29]. They are usually prepared from cereals such as Teff, maize, barley, millet or sorghum [26-28], but tej is prepared from honey [13]. Details of their preparation procedures and other important information have been reviewed [26-28].

2. EXPERIMENTAL

2.1. Chemicals and reagents

Analytical grade standards of s-triazine herbicides including atraton, desmetry and atrazine were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Stock standard solutions, containing 100 mg L^{-1} of each analyte, were separately prepared by dissolving appropriate weight of the standard in acetonitrile. Intermediate standard solution consisting of 10 mg L^{-1} of each analyte was also prepared in deionized water. Working standard solution was then prepared daily from the intermediate standard solution to optimize parameters affecting the HF-LPME procedure. All prepared solutions were stored under refrigeration below 4 ºC when not in use.

Organic solvents such as n-undecane, n-octanol, toluene, cyclohexane and dihexyl ether were all obtained from Sigma-Aldrich Chemie (Steinheim, Germany). HPLC grade methanol and acetonitrile were obtained from Carlo Erba Reactifs-SDS (Val de Revil, France). Sodium chloride (NaCl) and sodium hydroxide (NaOH) were purchased from BDH Chemicals Ltd (Poole, England). Hydrochloric acid (HCl) was obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Instrumentation and equipments

Chromatographic analyses of the target herbicides were carried out utilizing an Agilent 1200 series (Agilent Technologies, Waldbronn, Germany) high performance liquid chromatographic (HPLC) system equipped with a quaternary pump (flow range 0.2–10 mL min^{-1}), a vacuum degasser, a thermostated autosampler and column compartments as well as a multiple wavelength diode array detector (DAD). C_{18} analytical column (ZORBAX Eclipse XDB, 150 mm × 4.6 mm i.d., particle size 5 µm) from the Agilent Technologies was employed for chromatographic separations of the analytes. ChemStation B.02.01-SR1 was utilized for data acquisition and processing.

Hollow fiber membrane, 50/280 Accurel® PP polypropylene hollow fiber tubing: 50 µm wall thickness, 280 µm id, 0.1 µm pore size, which was obtained from (Membrana GmbH, Wuppertal, Germany) was used for sample preparation. BD micro fine 0.5 mL insulin syringes (with needle of 0.30 mm outer diameter and 8 mm length) obtained from BD Consumer Healthcare (Franklin Lakes, USA) was used to fill the acceptor solvent into the lumen of the hollow fiber and to also flush the solvent into autosampler vial after extraction. Adwa pH meter, Model 1020 from (Adwa Hungary Kft., Szeged, Hungary) was used for pH measurement. Orbital shaker, WSZ-100A model (Zhejiang, China) and an ultrasonic heater from (Dacon Laboratories, Ltd, St. Hove, East Sussex, UK) were also used for sample preparation.

2.3. Chromatographic conditions

Chromatographic separation of the target analytes was performed using a ternary mobile phase consisting of methanol (solvent A), water (solvent B) and acetonitrile (solvent C) at the ratio of 22:45:33 (v/v). Chromatographic elution were carried out at mobile phase flow rate of 0.5 mL min^{-1}, column temperature at 35 ºC, monitoring wavelength set at 235 nm and injection volume 5 µL. Peak area was utilized as an instrumental response.

2.4. Preparation of Supported Liquid Membrane and Extraction Procedure

The hollow fibers were manually cut into pieces of 20 cm length, with additional 0.5 - 1.0 cm free at each end to fold and seal the fiber [30]. Each piece of hollow fiber was used one time to avoid carry over effect. The fiber was immersed into the dihexyl ether for about 30 s to impregnate the pores of the hollow fiber wall so as to form the organic liquid membrane. Then, after flushing the lumen of the fiber with acceptor solution to remove organic solvent and air bubbles from the lumen, it was completely filled with accepter phase solution, 1.0 mol L^{-1} HCl). BD Micro-Fine syringe was used for flushing and filling of the lumen of the fiber with the accepter phase solution. Subsequently, the two ends of the fiber were folded and sealed with a piece of aluminum foil and connected to glass tubing to hang in the sample solution. Before using, it was rinsed with reagent water to remove extraorganic solvent from the surface. Finally, the prepared hollow fiber-supported liquid-membrane was introduced into 200 mL sample solution and then the content was shaken for 5 h at 200 rpm using an orbital shaker. After extraction was completed, the two ends of the sealed fiber were cut and then one of the end was connected to BD syringe needle, and whereas the other end was placed in the 200 µL insert, which was housed in 2 mL autosampler vial. The acceptor solution containing the target analytes was then flushed into the vial by pushing in the syringe plunger. Before, injecting into HPLC instrument the collected acidic acceptor solution was neutralized utilizing NaOH solution. Eventually, 5 µL of the obtained solution was injected into the HPLC system.

2.5. Locally brewed Ethiopian beverage samples

Four different types of Ethiopian locally brewed beverages (Tela) samples: Mulo, Filter, Nech and Keribe were prepared in home at Addis Ababa city, Addis Ababa, Ethiopia. From the prepared Tela samples, 1L was separately taken in glass bottles and transported to Analytical chemistry laboratory, Addis Ababa University Ethiopia; where they were stored below 4 ºC in dark until time of analysis, without any further sample treatment.

3. RESULT AND DISCUSSION

3.1. Optimization HF-LPME procedure

A three-phase HF-LPME procedure, which is based on the principle of supported liquid membrane (SLM), in which the organic (extraction) solvent is held in the pores of porous membrane supported by capillary forces was used for extraction of the target analytes [31-33]. Various experimental variables affecting the extraction efficiency, enrichment factor (EF) and selectivity of the analysis were investigated. These variables include the types of the extraction solvent, volume and pH of the sample (donor) and acceptor solutions, shaking (agitation) speed, extraction time and ionic strength of the sample solution [32]. During extraction, the target analytes are selectively transferred from the aqueous sample to another aqueous acceptor phase through the organic SLM present inside the

lumen of the fiber [34]. In this study, for optimization of experimental variables deionzed water sample was used by spiking with the target herbicides. Extraction was performed in triplicates and the extraction efficiency of the method under various conditions was evaluated using the EF.

3.1.1. Selection of membrane solvents

In HF-LPME, selection of proper membrane (extraction) solvent is important to quantitatively and selectively extract the target analytes. Pure or a mixture of organic solvents could be used as a membrane solvent [35]. Generally, the solvent chosen should be good affinity for the target analytes, low volatility to prevent solvent loss during the extraction, compatible with fiber and immiscible in acceptor and donor phases [32, 36]. In this study, five organic solvents including 1-octanol, toluene, *n*-undecane, dihexyl ether and cyclohexane were investigated to find the most suitable membrane solvents for extraction the target herbicides. It was observed that all the target herbicides were extracted when dihexyl ether was used as a membrane solvent. But, with other solvents none of the target analytes were extracted, except undecane, in which case only atrazine was extracted. Thus, dihexyl ether was selected for subsequent studies.

3.1.2. Effect of the donor phase volume

Volume of the donor phase is another important parameter that influences the extraction efficiency, particularly the EFs of the method [3, 18, 19, 37]. The effect of donor phase volume was assessed by varying the volume of the sample from 50-400 mL. As can be seen in Fig. 1, the EFs of the three target analytes increases with increasing donor phase volumes up to 200 mL and then, decrease at higher volumes. The increment in the enrichment factors of the analytes with the sample volume is expected, since larger sample volumes relatively contain high amount of analytes [37].

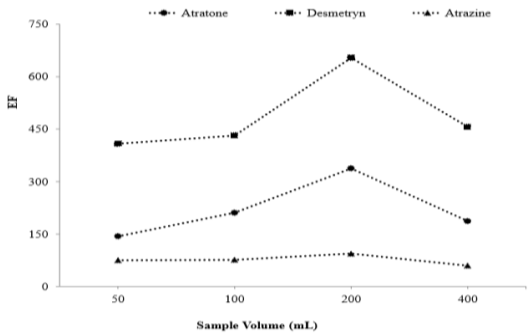

Fig. 1. Effects of the donor volume on the enrichment factor of the s-triazines. Experimental conditions: stirring rate, 150 rpm; extraction time, 1 h; extraction solvent, dihexyl ether.

On the other hand, the observed decrease in the enrichment factors at higher volume may be attributed to the inability of the shaker employed to thoroughly mix sample solution. Therefore, 200 mL of the sample solution was taken as the optimum values in subsequent experiments.

3.1.3. Effect of the donor phase pH

In pH gradient three-phase HF-LPME, pH of the sample solution is also another important factor influencing the extraction performance of the method [38]. For compounds containing acidic or basic functionalities, pH of the donor solution should be adjusted to transfer the analytes to their deionized forms, to decrease their solubility in the donor phase. On the other hand, pH of the acceptor phase should be adjusted to ensure that the analytes are present in their ionized forms, to promote their solubility in the acceptor phase [39]. In present study, the effect of pH of the sample was studied from 3 -7 and the obtained results are presented in Figure 2. The findings of the study demonstrated that the EFs of the analytes increase with increasing of pH of the donor phase up to pH 6 and then started to decline at higher pH values. Therefore, pH 6 was chosen as optimum pH for the subsequent experiments.

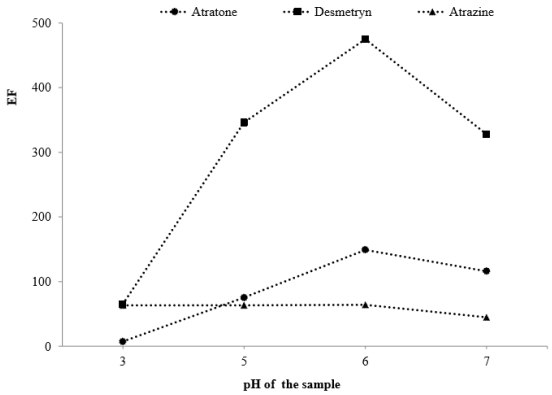

Fig. 2. Effect of the sample solution pH on enrichment factor of s-triazines. Experimental conditions: stirring rate, 150 rpm; extraction time, 1 h; volume of the sample solution, 200 mL; extraction solvent, dihexyl ether.

3.1.4. Effect of the shaking speed

Agitation (shaking) of sample solution accelerates the extraction processes by facilitating diffusion of the analytes through the interfacial layer of the hollow fiber [40]. Effect of agitation was assessed by varying shaking speed from 0–250 rpm. The obtained results showed the continuous increase of EFs of the target analytes with rising of the shaking speed up to 200 rpm. But, when higher shaking speed, i.e., above 200 rpm, was employed the stability of the hollow fiber was affected.

Thus, 200 rpm was chosen as optimum shaking speed for subsequent experiments.

3.1.5. Effect of extraction time

Three phases HF-LPME system involves two liquid-liquid interfaces and thus, the analytes requires enough time to diffuse through these interfaces to transfer into the acceptor phase [33, 39]. Thus, the influence of the extraction time on EFs of the analytes was tested from 60–600 min. The obtained results demonstrated that EFs of the target analytes increase with increasing of the extraction time up to 300 min (5 h) and then, started to gradually decrease on further increase of the extraction time (Figure 3). The observed results also revealed that extraction time has less effect on the EF of atrazine. As has also been reported in literature, in HF-LPME procedure, EF is expected to increase with the prolonged extraction time and reach maximum in the equilibrium stage [40]. On the other hand, the observed decrease in the EFs of the analytes at higher extraction time might be attributed to the saturation of the acceptor phase with the extracted analytes [21]. Therefore, 5 h was chosen as the optimum extraction time for further experiments.

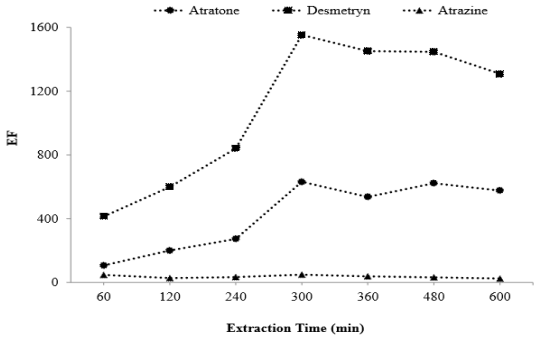

Fig. 3. Effect of the extraction time.

3.1.6. Effect of the ionic strength

Addition of salt into the sample solution decreases the solubility of the analytes in the donor phase and thus, enhances their transfer into the organic phase [18]. The effect of ionic strength on the extraction efficiency of the analytes was investigated by varying the concentration of the salt, NaCl, from 0-25 % (*w/v*). It was observed that EFs of the analytes increase with the amount of the salt added up to 20 % and then, exhibited reduction at higher concentrations. This decrement might be due to certain interaction between analytes and the salt that limit the movement of the analytes from the donor phase to the membrane solvent [41]. Thus, 20 % (*w/v*) NaCl was selected for further experiments.

3.2. Validation of the proposed method

3.2.1. Calibration curves and analytical performance characteristics

Analytical performance of the proposed HF-LPME method was evaluated by constructing external calibration curves. Calibration carves were established by extracting the spiked deionized water at five different concentration levels. Each concentration level was extracted in triplicate and each extract was then injected in duplicate. Calibration curves were plotted as peak areas versus the concentrations of the target analytes and were exhibited good linear dynamic ranges (LDR), as well as coefficients of determination of 0.990 or better. The limits of detections (LODs) and quantifications (LOQs) of the method were also investigated as the smallest concentration of the analytes yielding a signal-to-noise (S/N) ratio of 3 and 10, respectively. The analytical performance characteristics of the optimized method are presented in Table 1.

Table 1. Analytical performance characteristics of the proposed HF-LPME method.

Analyte	LDR (µg/L)	LOD (µg/L)	LOQ (µg/L)	R^2
Atratone	0.1-2	0.02	0.06	0.995
Desmetryn	0.1-2	0.02	0.05	0.998
Atrazine	0.1-2	0.04	0.12	0.990

3.2.2. Precision study

Intra-day (repeatability) and inter-day (intermediate) studies were employed to evaluate precision of the developed method. Intra-day precision was investigated by extracting six deionized water samples spiked with the mixture of the standard solution containing 2 µg L^{-1} of each analyte, in two batches within one day. The inter-day precision was also tested by extracting the spiked deionized water samples at the same concentration level earlier used in intr-day precision study, for six consecutive days. The findings of the intra- and inter-day precision studies, which are expressed in terms of relative standard deviations (% RSD) of peak area of the target analytes are presented in Table 2. As can be seen the proposed method exhibited good precisions, i.e., RSD less than 8.00%, which is in the acceptable precision range for analysis of pesticides residues from different matrices [42].

Table 2. Intra- and inter-day precisions of the proposed method (%RSD) for the spiked deionized water samples.

Analyte	Intra-day (n = 6)	Inter-day (n = 6)
Atratone	6.24	5.78
Desmetryn	6.59	5.35
Atrazine	5.92	7.64

3.2.3. Selectivity study

Selectivity of a method refers to the extent to which a proposed method could be used to determine the target analyte/s, without being interfered by other components that are available in the matrix [43]. In this study, selectivity of the proposed method was investigated by comparing the chromatograms of the blank (unspiked) analytes free locally brewed beverage samples with their corresponding spiked samples. Figure 4 (i – iv) shows typical chromatograms of the blank (unspiked) and spiked locally brewed beverages with the target herbicides. As can be seen from the chromatograms, no interferences were observed at the retention times of the target analytes for all the studied beverage samples. Generally, the observed findings demonstrated that the proposed HF-LPME method has good selectivity for the determination of the residual levels of the target herbicides by HPLC-DAD in Ethiopian locally brewed beverages and other related matrices.

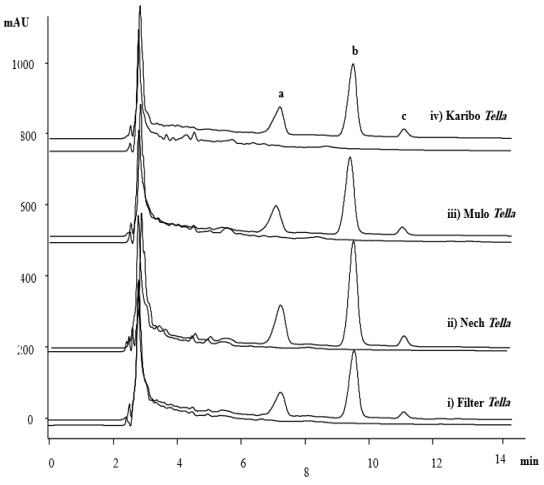

Fig. 4. HPLC-DAD chromatograms of unspiked and spiked samples of locally brewed Ethiopian beverages with 50 µg L^{-1} of the three triazines standard mixture: a) atratone b) desmetryn and c) atrazine.

3.2.4. Applications and recovery studies

The matrix effect and applicability of the developed method was investigated by performing relative recovery (%RR) studies utilizing four different types of locally brewed beverages, namely; Mulo, Karibo, Nech Tella and Filter samples. For %RR studies, each of these samples was spiked with the target analytes at the concentration level previously used for the precision studies. For each beverage, one blank and two spiked samples were extracted using the proposed HF-LPME procedures and analyzed by HPLC-DAD. It was observed that none of the target analytes were detected in these samples. %RRs, which were determined as the ratio of the peak area of the target analytes obtained from spiked beverage samples to the peak area of the spiked deionized water sample [32], were in the range of 51–107% with RSDs varying from 0.7–8.5% as indicated in Table 3. It was observed that acceptable %RR were obtained for atratone and desmetryn, whereas, atrazine exhibited smaller %RR, indicating the influence of matrix on its extraction efficiency.

Table 3. Relative recoveries of pesticides determined in beverage samples using the proposed method.

Beverage Sample	Relative Recovery (RSD, n = 3)		
	Atratone	Desmetryn	Atrazine
Nech Tela	94 (0.7)	84 (2.7)	51 (7.4)
Mulo Tela	102 (3.9)	99 (3.9)	68 (8.5)
Filter Tela	86 (5.8)	83 (6.1)	55 (7.0)
Karibo Tela	107 (5.8)	107 (0.6)	76 (6.3)

4. CONCLUSION

A three phase HF-LPME method combined with HPLC-DAD has been developed as simple and attractive alternative for analysis of three trazine herbicides in locally brewed beverages of Ethiopia. Different parameters affecting the extraction efficiencies of the target analytes such as types of extraction solvent, volume and pH of the donor solution, shaking speed, extraction time and ionic strength were investigated and the optimum conditions were established. Under the optimum condition the method exhibited good linearity with coefficients of determination r^2 0.990 or better. It has also demonstrated large enrichment factors, low solvent consumption and good selectivity for analysis of the target anlytes. The precision studies of the method were also acceptable (i.e., RSD less than 8.00) and satisfactory relative recoveries were obtained for the studied analytes with exception of atrazine in Nech and Filter Tela, which were relatively showed lower %RR. However, the selectivity and precision of the analyte in these samples are acceptable. Generally, the obtained results indicated that the proposed method could be utilized as alternative method for extraction/preconcentration and determination of s-triazine herbicides in Ethiopian locally brewed beverages and other similar matricies.

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