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Switchable solvent based liquid phase microextraction of copper(II): optimization and application to environmental samples

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Abstract

A switchable solvent based liquid phase microextraction (SS-LPME) procedure has been established for preconcentration of copper prior to its determination by microsampling flame atomic absorption spectrometry (FAAS). Triethylamine (TEA) protonated triethylamine carbonate (P-TEA-C) as green and cheap switchable solvent was used in the presented work. Cu(II)-1-(2-pyridylazo)-2 naphthol (PAN) complex was extracted to triethylamine phase by converting protonated triethylamine carbonate to triethylamine. The experimental conditions were comprehensively studied and optimized. The limit of detection (LOD) and repeatability (RSD %) of the method were $1.80 \mu\text{g L}^{-1}$ and 3.8%, respectively. The accuracy of method was evaluated by analyzing certified reference materials (TMDA-64.2 fortified water, TMDA-53.3 fortified water, TMDA-51.3 fortified water, 1573a Tomato Leaves, INCT-OBTL-5 Oriental Basma Tobacco Leaves and NCS ZC 8100 2b Human Hair) and addition-recovery tests. The SS-LPME-FAAS method was also applied for the determination of trace amounts of copper in water, food and hair samples.

Keywords: switchable solvent based liquid phase microextraction, copper, triethylamine, protonated triethylamine carbonate, microsampling flame atomic absorption spectrometry.

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Introduction

Most of analytical methods are often multistep processes which involve reactions, extractions, separations, preconcentration and determinations.¹⁻³ The biggest obstacle for the development of green analytical methods is the utilization of specific and green solvents for specific analytical application.⁴ For example, the preconcentration and extraction of trace analytes from matrix medium in a sample is one of the most important issues worked by the analytical chemistry. Analytes and matrix component often have solubility, meaning a different polarity solvent is required to extract analyte components from matrix components of a sample.^{5, 6} The selection of the “right” solvent is critical not only for a successful extraction but also for the development green analytical methods.⁷ The conventional answer to making analytical methods more green is to reduce waste through recycling and reduced waste, eliminate to consumption of toxic solvents from analytical procedures.^{8, 9} But this doesn't solve the main problem that specific solvents are still necessary for a specific application. Imagine a solvent that can transform itself, changing its properties to meet multiple applications. This is not science dream, such solvents are a reality.

A new generation solvents called “switchable” or “smart” solvents (SS) was developed by Jessop et al..¹⁰ Switchable solvents are defined as “a system in which a non-ionic liquid converts to an ionic liquid upon exposure to an atmosphere of carbon dioxide (CO₂) and then reverts back to its non-ionic form when exposed to nitrogen, inert gas and addition of sodium hydroxide” Because of the reversibility of the reaction, the changed solvent can easily be brought back to its original state.¹¹⁻¹⁶

The switchable solvents consist of an amine dissolved in water. The non-ionic form of SS has very limited miscibility with water in the absence of CO₂ but complete miscibility with water in the ionic form of SS. The change in miscibility is caused by a chemical reaction of

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3 the CO₂ and water, giving a water-soluble carbonate salt of the protonated amine. The SS
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5 must therefore be sufficiently basic to be protonated by carbonic acid. CO₂ is used as the
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7 trigger for the switching process because it is inexpensive, non-toxic, benign, and easily
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9 removed.¹³⁻¹⁸ The development of these type recyclable solvents is phenomenal to achieving
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11 chemical applications that are cheap, safe and environmentally conscious and these solvents
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13 offer new possibilities for a “greener” process design and can be considered under the Green
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15 Chemistry. The development of switchable solvents followed current publications mostly
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17 focus on exploiting the wide range of applications such as extraction, separation and reaction
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19 tasks.¹³⁻¹⁸
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23 In recent years, the scientists have developed some simple, cheap and fast separation
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25 and preconcentration methods called liquid-phase microextraction (LPME) technique, The
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27 technique was used for different ways such as dispersive liquid–liquid microextraction
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29 (DLLME)¹⁹, ionic liquid-based dispersive liquid–liquid microextraction (IL-DLLME)²⁰,
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31 ultrasound-assisted dispersive liquid–liquid microextraction (UA-DLLME)²¹, vortex-assisted
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33 dispersive liquid–liquid microextraction (VA-DLLME)²² single drop microextraction
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35 (SDME)²³ and ion pair-based surfactant-assisted microextraction (IP-SAME)²⁴. In this field,
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37 the search of alternative and novel solvents for separation media has become a priority and
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39 much attention.
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43 The scope of this work is to highlight the potential of the emerging area of switchable
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45 solvents for microextraction of trace metal ions from environmental samples. The present
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47 work deals with the quantification of copper in water, food and hair samples by using
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49 switchable solvent based liquid phase microextraction with micro sampling flame atomic
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51 absorption spectrometer (SS-LPME-FAAS).
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Experimental

Apparatus

An Analyst 300 Model flame atomic absorption spectrometer (Norwalk, CT, USA) including air–acetylene flame and equipped with a hollow cathode lamp and Zeeman background correction was used. The instrumental parameters were adjusted as follows: wavelength 324.8 nm, slit width: 0.7 nm, lamp current: 15.0 mA, burner height: 6.5 mm, fuel gas : acetylene, support gas : air, flow rate for acetylene: 2 mL/min and flow rate for air: 17 mL/min. The absorbance measurements were performed with the continuous aspiration mode of FAAS.

The samples were aspirated to the nebulizer of FAAS by using handmade micro injection system, which consist of a mini home-made Teflon funnel with an Eppendorf Pipette.²⁵ The Teflon funnel was connected to the nebulizer of FAAS with capillary tubing. A 100 μ L of extraction phase taken with Eppendorf pipette was injected to the micro-injection unit and peak heights were measured as signals.²⁵

All pH measurements were carried out using a Sartorius PT-10 pH meter (Germany) equipped with a glass electrode. A centrifuge (ALC PK 120 Model, Buckinghamshire, England) was used for phase separation.

Solutions and reagents

Ultrapure water obtained from a MilliQ Direct-16 purification system (18.2 M Ω cm, Millipore) and analytical grade reagents were used throughout. CO₂ (Dry ice) was provided by Ates Company (Kahramanmaras, Turkey). Triethylamine, NaOH, Concentrated 30 % (v/v) H₂O₂ and 65 % HNO₃ were purchased from E. Merck Company (Darmstadt, Germany). A 0.05 % of 1-(2-pyridylazo)-2 naphthol (PAN) solution obtained from E. Merck, Darmstadt was prepared with using ethanol.

Synthesis of switchable solvent

In the synthesis of protonated triethylamine carbonate that completely miscible with ultrapure water from triethylamine, we took advantage of dry ice as non-toxic, benign and inexpensive. The synthesis of protonated triethylamine carbonate is based on the reaction of CO₂ with triethylamine in an equal volume mixture of triethylamine and water. 200 mL of triethylamine and 200 mL of ultrapure water were poured into a 1 L beaker and stirred at room temperature. At the same time CO₂ (Dry ice ~20 g) was added gradually in the beaker. After completely dissolution of CO₂, the solubility of triethylamine increased and cloudy phase was shown. The addition of dry ice was repeated for twenty times to ensure the complete protonation of triethylamine and until obtain a single protonated triethylamine carbonate phase. 400 mL of the protonated triethylamine carbonate solution (extraction solution) can be easily synthesized and this volume allows the using of more than 300 experiments since each one needs only 1.0 mL of the extraction solution. The synthesized switchable solvent was stable at room temperature at least for two months. The quantitative results were obtained with synthesized switchable solvent under optimal working conditions after two months its preparation.

Switchable solvent based liquid phase microextraction procedure

A schematic diagram of the switchable solvent based liquid phase microextraction procedure is shown in Figure 1. A 10 mL sample solution containing 40 µg L⁻¹ of Cu(II), 2 mL of pH 8.0 NH₃/NH₄Cl buffer solution and 0.3 mg 1-(2-pyridylazo)-2 naphthol as complexing agent were mixed in the 50 mL conical bottom centrifuge tube and waited for 2 min. for the formation of Cu(II)-PAN complex. Firstly, 1.0 mL of protonated triethylamine carbonate was quickly injected to in the centrifuge tube by using a

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3 injector. Then, 2.0 mL of 10 M NaOH solution was injected and a cloudy solution appeared in
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5 the centrifuge tube. At this stage, protonated triethylamine carbonate was converted to
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7 triethylamine and Cu(II)-PAN complex in the aqueous phase was extracted into the fine
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9 droplets of triethylamine in a few seconds. After extraction, to accelerate the phase separation,
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11 these droplets were collected on the surface of the aqueous phase by centrifugation at 4000
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13 rpm for 10 min. Then the triethylamine phase, which was approximately 0.4 mL, was
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15 separated from aqueous phase and completed its volume 0.6 mL with concentrated HNO₃.
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17 Finally, the copper concentration was determined with flame atomic absorption spectrometry
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19 in continuous aspiration mode by using a handmade microinjection system. In this system,
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21 100 µL of the extraction phase was introduced the microinjection system coupled to FAAS
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23 nebulizer.
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30 **Sample collection and preparation**

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32 The water samples were obtained from Kayseri, Turkey. The samples were filtered
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34 through 0.45 µm pore size membrane filters immediately after sampling. Finally, the
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36 developed microextraction procedure was applied to these samples and certified reference
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38 materials including TMDA-64.2 fortified water, TMDA-53.3 fortified water and TMDA-51.3
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40 fortified water. The copper concentration in last volume was determined with microsampling
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42 FAAS.
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45 The chili powder, black pepper and peppermint samples were purchased from Market
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47 in Kayseri, Turkey. The green pepper, tomato and cucumber samples were collected from
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49 Yahyali -Kayseri,
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52 Human hair samples were taken from male living in Kayseri, Turkey. The collected
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54 green pepper, tomato, cucumber and hair samples were washed with ultrapure water, oven-
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56 dried at 100 °C for 24 h. and were homogenized by using an agate mortar and pestle. An open
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3 digestion-vessel method was used in order to digest the all samples. For this digestion
4 method, various amounts of samples and certified reference materials (Tomato Leaves, INCT-
5 OBTL-5 Oriental BasmaTobacco Leaves and NCS ZC 8100 2b Human Hair) were separately
6 weighed into beakers. Concentrated HNO₃ (15 mL) was added into each beaker and heated on
7 a hot plate at 100 °C until dryness and the residues in the beakers were then cooled. Then, ten
8 mL concentrated HNO₃ and 5 mL H₂O₂ added and again heated to dryness. The mixture was
9 dissolved in water, filtered and used as real samples for the developed microextracton method.
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23 **Results and discussion**

24 **Effect of pH**

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27 The pH of analyte solution plays a unique role on the formation of complexes with
28 sufficient hydrophobicity and subsequent extraction.²⁶ The complex formation of PAN with
29 transition metal ions especially with Cu(II) is seen approximately after pH 7.0.²⁷ Hence, in
30 this study, effect of pH on the extraction efficiency was investigated with in the range of pH
31 5.0 to 11.0 and the results were shown in Fig. 2. The extraction recovery was more than 95%
32 in the pH range of 8.0–9.0. Hence, pH 8.0 was used for subsequent work and real sample
33 analysis.
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45 **Effect of 1-(2-pyridylazo)-2 naphthol (PAN) amount**

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47 PAN forms very stable and hydrophobic complexes rapidly with metal species
48 especially with Cu(II) around basic pH, which provide solubility of metal complex in
49 extraction phase.²⁷ Hence PAN was selected as complexing agent for present work.. The
50 variations in the recoveries as a function of the amount of PAN in the range of 0-0.4 mg were
51 investigated. The effect of the PAN amount on the recovery is shown in Fig. 3. The
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3 experimental results showed that recovery increased between 0 and 0.2 mg then remained
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5 quantitative with increasing amount of PAN. Therefore, 0.3 mg of PAN was chosen in this
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7 work.
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10 11 **Effect of volume of protonated triethylamine carbonate**

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14 The synthesized protonated triethylamine carbonate (P-TEA-C) is miscible water form
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16 of switchable solvent while triethylamine (TEA) is immiscible form of switchable solvent. CO₂
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18 was used as the trigger to convert TEA form to P-TEA-C form because it is non-toxic, benign,
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20 inexpensive and easily removed, while NaOH was used to convert P-TEA-C form to TEA
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22 form because it is readily available under laboratory conditions and inexpensive. Due to the
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24 their switchable properties, TEA/ P-TEA-C solvent pair was used for the extraction of Cu(II)-
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26 PAN complex from sample solution. The effect of the volume of P-TEA-C on the recovery of
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28 Cu(II) was studied by using a series of sample solution containing 0.3 mg PAN and different
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30 volumes of the extraction solvent (between 0.25 mL-1.25 mL) to found best extraction solvent
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32 volume. The extraction efficiency increases with increasing the volume of P-TEA-C from
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34 0.25 to 1.0 mL (Fig 4). However, the extraction efficiency was constant when the volume of
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36 P-TEA-C was larger than 1.0 mL. 1.0 mL was selected as the optimal extraction solvent
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38 volume.
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45 **Effect of NaOH volume**

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47 The removing of CO₂ from hydrophilic protonated triethylamine carbonate causes the
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49 two phases including water and triethylamine phases. For this purpose, 10 M of NaOH was
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51 used to convert the P-TEA-C form of switchable solvent to hydrophobic TEA phase and, at
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53 the same time, extract the Cu(II)-PAN complex from water phase to TEA phase. The effects
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55 of volume of 10 M NaOH were investigated in the range of 0.5-4.0 mL. The results are
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3 depicted in Figure 5. The recovery increased until 2.0 mL of 10 M NaOH and then decreased
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5 with increasing volume of NaOH. It should be noted that the excess of NaOH, which is
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7 remaining unreacted with protonated triethylamine carbonate, may caused a change of pH
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9 sample solution and may broke the Cu(II)-PAN complex formed. When the excess of NaOH
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11 was added, the cloudy system was not well formed, hence the recovery decreased. Based on
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13 the obtained experimental results, 2.0 mL of 10 M NaOH was used in all subsequent
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15 experiments.
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20 21 **Effect of sample volume**

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23 To determine low concentrations of analytes in the samples, a high preconcentration
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25 factor is requested for liquid phase microextraction techniques by using low sample volume.
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27 Hence, the sample volume is important parameter to be optimized. The effect of the sample
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29 volume on the efficiency of the suggested microextraction was investigated for a range of 10–
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31 30 mL sample volume. Cu(II) were quantitatively (>95%) recovered below 15 mL. Therefore,
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33 a preconcentration factor of 25 was obtained ratio of the 15 mL of the sample to 0.6 mL of
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35 final volume.
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40 41 **Effect of coexisting ions**

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43 The other potentially interfering ions in real samples may show interference effect for
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45 the accurate determination of metal ions at trace levels.²⁸⁻³⁵ The effects of foreign ions was
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47 investigated with the purpose of identifying the potentials using model solutions containing
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49 40 $\mu\text{g L}^{-1}$ Cu(II) (Table 1). The results show that Na^+ , K^+ , F^- and Cl^- at the ratio of 1:150000,
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51 Mg^{2+} and Ca^{2+} at the ratio of 1:15000 and SO_4^{2-} at the ratio of 1:45000 showed no
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53 interference with the formation and extraction of Cu(II)-PAN complex; Zn^{2+} at the ratio of
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3 1:300, Ni²⁺, Fe³⁺, Hg²⁺, Ir³⁺ and Pd²⁺ at the ratio of 1:150 and Co²⁺, Cd²⁺, Bi³⁺ and Cr³⁺ at the
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5 ratio of 1:75 did not interfere.
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8 9 10 **Analytical performance**

11 The linear calibration curve was obtained as equation $Abs. = 0.0544C + 0.0018$, $R^2 =$
12 0.994 (where Abs is the absorbance and C is the concentration of Cu(II), mg L⁻¹). The
13 preconcentration factor was found as 25 by using ratio of the 15 mL of the sample to 0.6 mL
14 of final volume. The enhancement factor, which was calculated as the ratio between the slope
15 of a calibration curve prepared from sample solutions submitted to the developed
16 microextraction method, and that obtained of a calibration curve were not submitted to the
17 microextraction procedure, was 17.6. The relative standard deviation (RSD) for seven
18 replicates of 40 µg L⁻¹ of Cu(II) was 3.8%. The limit of detection (LOD) and limit of
19 quantification (LOQ) were calculated by 3Sb/m and 10Sb/m respectively. The standard
20 deviation of the blank, Sb was equal to 8.2×10^{-4} and the slope of the calibration curve after
21 extraction, m= 0.0544 µg mL⁻¹. The LOD and LOQ (n = 7) was found to be 1.80 µg L⁻¹ and
22 5.94 µg L⁻¹, respectively. Consumptive index (CIn) was 0.85 (calculated as the ratio of
23 sample volume in milliliters to enhancement factor). The frequency of analysis was at least 16
24 samples per hour.
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45 **Validation of the SS-LPME method**

46 Due to the biological and environmental significance of copper, several samples of
47 water, food and hair were analyzed for validation and applicability of the proposed method.
48 The accuracy of the proposed method was evaluated by analysis of certified reference
49 materials (TMDA-64.2 fortified water, TMDA-53.3 fortified water, TMDA-51.3 fortified
50 water, 1573a Tomato Leaves, INCT-OBTL-5 Oriental Basma Tobacco Leaves and NCS ZC
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3 8100 2b Human Hair) and addition-recovery experiments for food and hair samples (means of
4 recovery experiments, different amounts of copper were added to the sample solutions and
5 subsequently assayed by the developed procedure). All the obtained results for certified
6 reference materials and addition-recovery experiments are presented in Table 2 and Table 3,
7 respectively. The results for certified reference materials were in agreements with the certified
8 values. The results for addition-recovery experiments showed that recoveries of the method
9 for copper in food and hair samples were from 97 to 105 % with RSD (n = 3) less than 6.0 %.
10 The obtained all results for validation of the SS-LPME demonstrated that the developed
11 method was not affected samples matrices and applicable for determination of copper in
12 water, food and hair samples.
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25 26 27 **Applications**

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29 The suggested SS-LPME procedure was successfully applied for the determination of
30 Cu in water, food and hair samples obtained from Kayseri, Turkey. The copper concentrations
31 in samples were given Table 4.
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38 **Comparison with the other methods**

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40 A comparison of the SS-LPME method with other reported preconcentration methods
41 coupled with FAAS is given in Table 5. In comparison with the other methods, the SS-LPME
42 shows a comparatively low detection limit ($1.80 \mu\text{g L}^{-1}$) and a high enhancement factor (17.6)
43 for Cu in a high extraction frequency (at least 16 samples per hour) short time.
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Conclusions

The determination of copper in water, food and hair samples by switchable solvent based liquid phase microextraction combined with microsampling FAAS was shown as a green, cheap, simple and efficient method. CO₂ and NaOH were non-toxic, benign, inexpensive and easily found chemicals in laboratory conditions. The main advantages of using of SS for microextraction studies are that allows the extraction of the analytes in a homogeneous phase without dispersive solvent and easy operation without additional apparatus and experimental steps. We took benefits of these chemicals by using CO₂ (Dry ice) at atmospheric pressure to switch the solvent (triethylamine) to its hydrophilic form (protonated triethylamine carbonate), and NaOH to switch it back again triethylamine phase and also extract Cu(II)-PAN complex. The other advantages of the method were; (I) the synthesis of protonated triethylamine carbonate was simple and it can be used for more than 300 experiments for at least 10 months. (II) No need organic solvent for dispersion of extraction solution to aqueous phase and because of this advantage no produce secondary waste. (III) It can be used without recourse to a special apparatus or additional handling requirements like vortex and ultrasonic bath in the other liquid phase based microextraction methods to improve the interaction between analytes and extraction phase. (IV) No need extra complicated and time consuming steps like heating, cooling, pressure assistance, air assistance, addition of salt for formation of extraction phase.

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Figure captions

Fig. 1. Graphical representation of the switchable solvent based liquid phase microextraction method (SS- LPME).

Fig. 2. Influence of pH on extraction efficiency of Cu(II). PAN: 0.3 mg, Volume of the P-TEA-C: 1.0 mL, Volume of the 10 M NaOH solution: 2.0 mL (N=3).

Fig. 3. Influence of the PAN amount on extraction efficiency Cu(II). pH: 8.0, Volume of the P-TEA-C: 1.0 mL, Volume of the 10 M NaOH solution: 2.0 mL (N=3).

Fig. 4. Effect of the extractant volume on extraction efficiency Cu(II). pH: 8.0, amount of PAN: 0.3 mg, Volume of 10 M NaOH solution: 2.0 mL (N=3).

Fig. 5. Effect of volume of 10 M NaOH on extraction efficiency Cu(II). pH: 8.0, amount of PAN: 0.3 mg, Volume of the P-TEA-C: 1.0 mL (N=3).

Table 1. Influence of some foreign ions on extraction efficiency of Cu(II). pH: 8.0, Amount of PAN: 0.3 mg Volume of the P-TEA-C: 1.0 mL, Volume of the 10 M NaOH solution: 2.0 mL (N=3).

Ion	Added as	Concentration mg L ⁻¹	Matrix ion/Cu(II)	Recovery, %
Na ⁺	NaNO ₃	5000	150000	95±4
K ⁺	KCl	5000	150000	98±4
Ca ²⁺	Ca(NO ₃) ₂ .4H ₂ O	500	15000	100±0
Mg ²⁺	Mg(NO ₃) ₂ .6H ₂ O	500	15000	100±0
Zn ²⁺	Zn(NO ₃) ₂ .6H ₂ O	10	300	96±4
Co ²⁺	Co(NO ₃) ₂ .6H ₂ O	2.5	75	101±4
Cd ²⁺	Cd(NO ₃) ₂ .4H ₂ O	2.5	75	94±3
Bi ³⁺	Bi (NO ₃) ₃	2.5	75	100±1
Cr ³⁺	Cr(NO ₃) ₃ .9H ₂ O	2.5	75	95±5
Ni ²⁺	Ni(NO ₃) ₂ . 6H ₂ O	5	150	100±2
Fe ³⁺	Fe(NO ₃) ₃ 9H ₂ O	5	150	105±2
Hg ²⁺	Hg(NO ₃) ₂ .H ₂ O	5	150	99±3
Ir ³⁺	IrCl ₃	5	150	98±5
Pd ²⁺	Pd(NO ₃) ₂	5	150	97±3
Cl ⁻	KCl	5000	150000	98±4
SO ₄ ²⁻	Na ₂ SO ₄	1500	45000	105±0
F ⁻	NaF	5000	150000	96±4

Table 2. The analysis results of certified reference materials. pH: 8.0, Amount of PAN: 0.3 mg Volume of the P-TEA-C: 1.0 mL, Volume of the 10 M NaOH solution: 2.0 mL (N=5).

	Certified Value, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	Recovery, %
TMDA-64.2 Fortified water	274	287 \pm 13 ^a	105
TMDA-53.3 Fortified water	308	294 \pm 13	95
TMDA-51.3 Lake Ontario water	89.2	93 \pm 2	104
	Certified Value, mg kg^{-1}	Found, mg kg^{-1}	Recovery, %
1573a Tomato leaves	4.70 \pm 0.14	4.73 \pm 0.10	101
Oriental basma tobacco leaves (INCT-OBTL-5)	10.1 \pm 0.4	9.7 \pm 0.1	96
NCS ZC 8100 2b Human hair	33.6 \pm 2.3	35.0 \pm 1.6	104

^a Mean \pm standard deviation.

Table 3. Addition and recovery test for SS-LPME of copper in food and hair samples. pH:

8.0, Amount of PAN: 0.3 mg Volume of the P-TEA-C: 1.0 mL, Volume of the 10 M

NaOH solution: 2.0 mL (N=5).

Samples	Added μg	Found μg	Recovery %	Samples	Added μg	Found μg	Recovery %
Green pepper	0.00	1.27±0.05 ^a	-	Tomato	0.00	1.31±0.05	-
	0.25	1.52±0.05	100		0.50	1.87±0.05	103
	0.50	1.72±0.05	97		0.75	2.07±0.09	100
Peppermint	0.00	0.78±0.08	-	Human hair	0.00	0.42±0.00	
	0.50	1.34±0.12	105		0.50	0.89±0.00	97
	1.00	1.77±0.05	99		1.00	1.39±0.04	98

^a Mean ± standard deviation.

Table 4. The determination of copper in water, food and hair samples by using the developed SS-LPME method. pH: 8.0, Amount of PAN: 0.3 mg Volume of the P-TEA-C: 1.0 mL, Volume of the 10 M NaOH solution: 2.0 mL (N=5).

Samples	Concentration, $\mu\text{g L}^{-1}$
Dam water	62.3 \pm 4.0 ^a
Underground water	BDL ^b
Waste water-I	1298 \pm 36
	Concentration, $\mu\text{g g}^{-1}$
Cucumber	10.3 \pm 1.8
Tomato	1.9 \pm 0.0
Chili powder	5.7 \pm 0.2
Black pepper	3.8 \pm 0.2
Hair sample-I	10.7 \pm 1.0
Hair sample-II	11.3 \pm 1.0

^a Mean \pm standard deviation.

^b BDL: Below the detection limit

Table 5. Comparison of the SS-LPME with other methods for the determination of copper in real samples with FAAS

Method	^a LOD, $\mu\text{g L}^{-1}$	^b PF or ^c EF	RSD, %	Sample	Ref.
Hollow fiber supported liquid membrane microextraction	4	551	6	Water	36
Ultrasound-assisted ionic liquid based dispersive liquid-liquid microextraction	1.9	56	3.8	Water	37
Dispersive liquid-liquid microextraction	0.45	136.6	3.3	Water	38
Cloud Point Extraction	0.6	30	1.0	Environmental samples	39
Solid Phase Extraction	1.9	225	2.1	Foods	40
Dispersive liquid-liquid microextraction	3	42	5.1	Water	41
Liquid-liquid microextraction	4	551	6	Water	42
Dispersive liquid-liquid microextraction	0.1	122	3.9-5.7	Food	43
Dispersive liquid-liquid microextraction	0.04	560	2.1	Water	44
Solid-phase extraction-flow injection-flame atomic absorption spectrometry	0.93	43	1	Water	45
Solidified floating organic drop microextraction	0.18	541	2.7	Water	46
Dispersive liquid-liquid microextraction based on solidification of floating organic drop	0.1	122	3.9-5.7	Cereal	47
Switchable solvent based liquid phase microextraction	1.80	25	3.8	Water, food and hair	This study

^a Limit of detection, ^b Preconcentration factor, ^c Enhancement factor

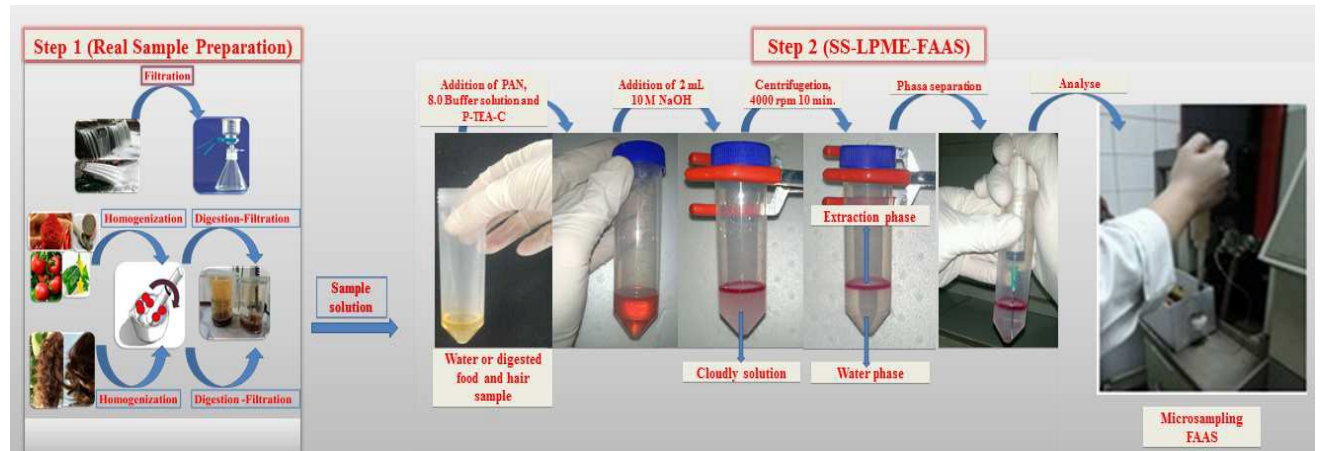


Fig. 1.

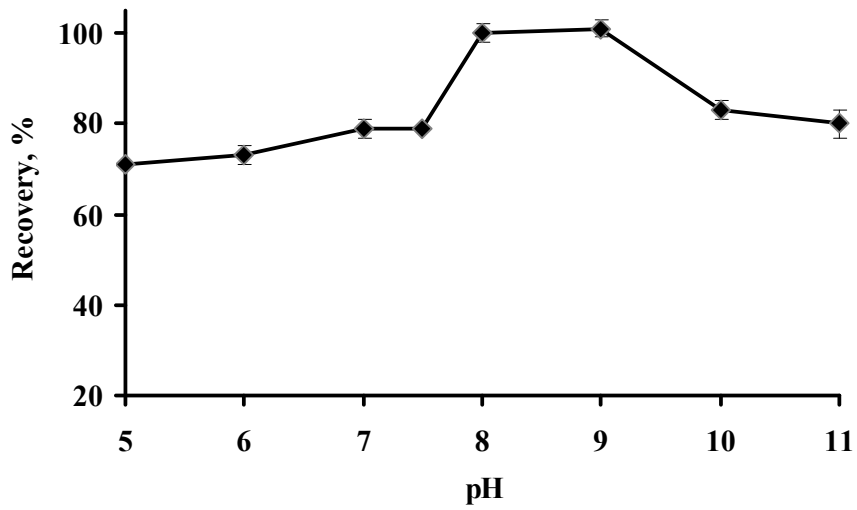


Fig. 2.

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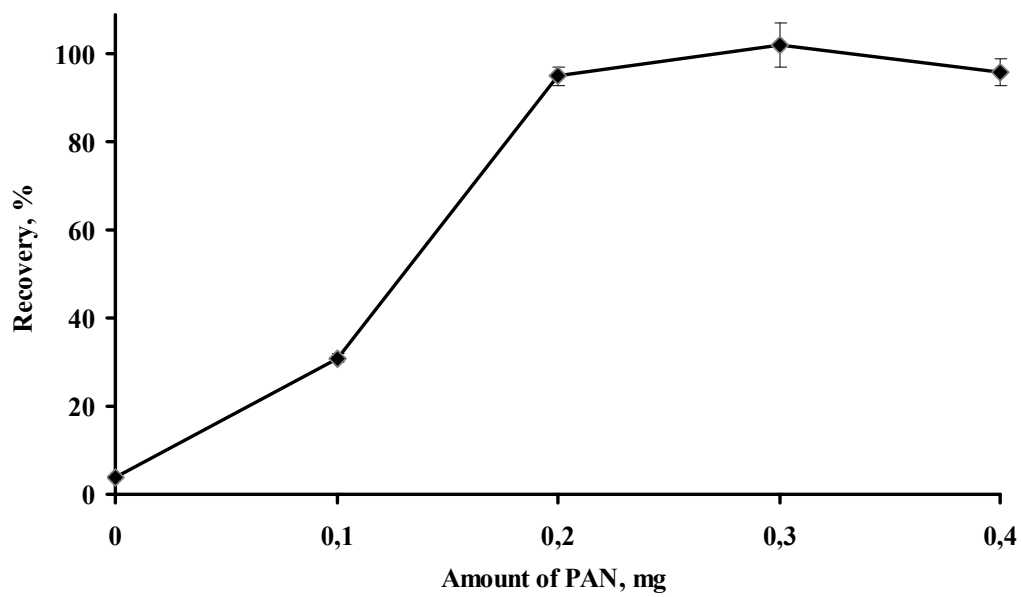


Fig. 3.

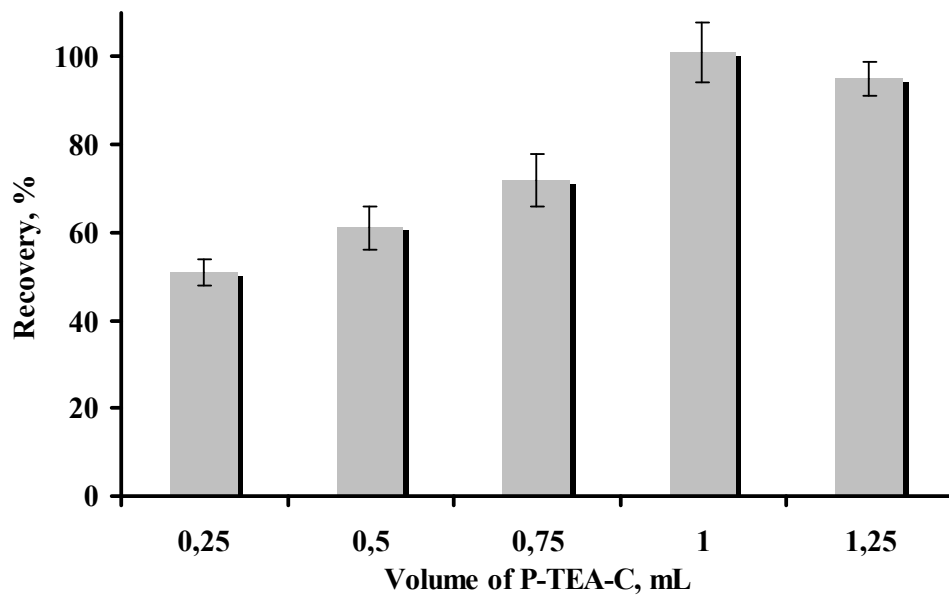


Fig. 4.

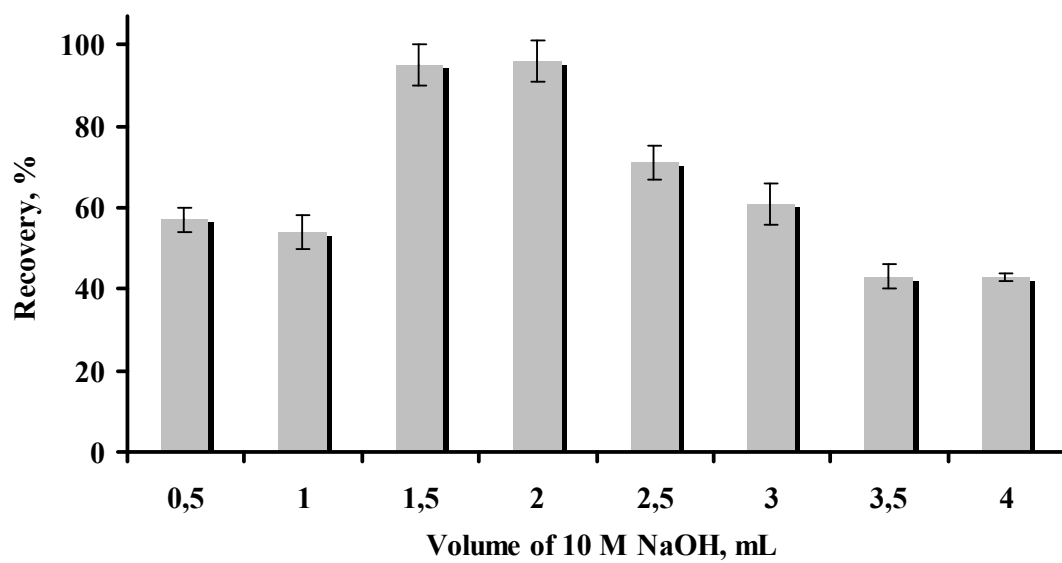
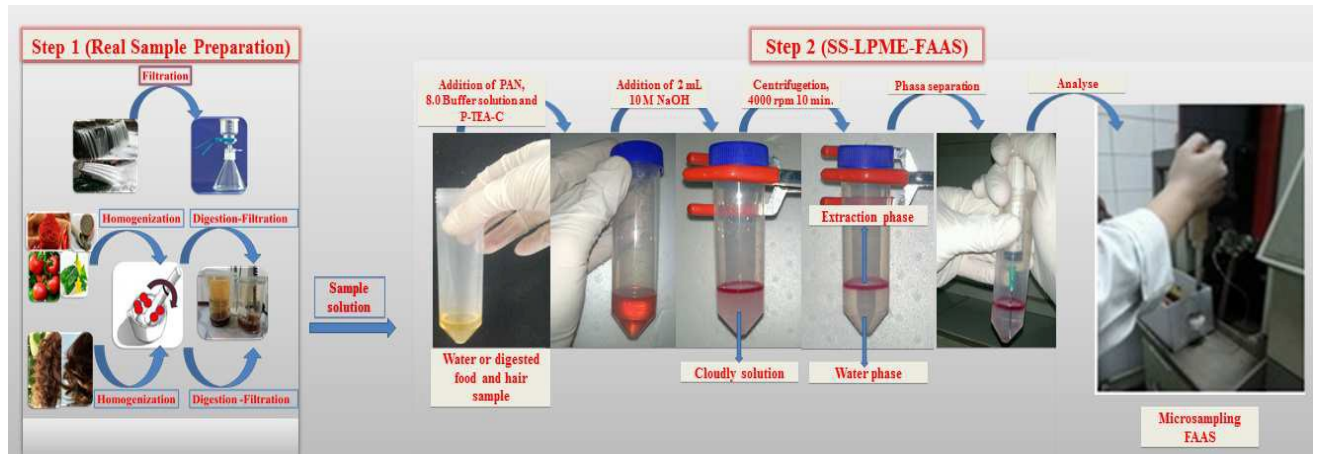


Fig. 5.



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