Iranian Journal of Analytical Chemistry
Volume 10, Issue 1, March 2023 (80-88) Original Research Article

مجله ایرانی شیمی تجزیه
دوره ۱۰، شماره ۱، فروردین۱۴۰۲ (۸۸-۸۰)

Biological Application of Dispersive Magnetic Solid Phase Extraction Using Fe_3O_4@Cuo&GO Nanocomposite and Ion Mobility Spectrometry: Determination of Aspirin

Farideh Shamsi , Ali Sheibani* , M. Reza Shishehbore

Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran

Received: 16 May 2023 **Accepted:** 25 June 2023
DOI: 10.30473/ijac.2023.67944.1269

Abstract
In this study, a dispersive magnetic solid phase extraction (DMSPE) was described by combining graphene oxide (GO) with Fe_3O_4 and CuO (Fe_3O_4@CuO&GO) for extraction and preconcentration of aspirin (ASP) in biological samples. The morphology and structure of the prepared nanocomposite was characterized and analyzed by XRD, SEM and FTIR techniques. Ion mobility spectrometry (IMS) method equipped to a corona discharge ionization source was exploited to determine ASA. The extraction parameters (desorption solvent, pH, adsorbent amount, extraction time and temperature) and also the operational parameters of IMS were investigated and optimized. Under the optimum conditions, the DMSPE–IMS method provided a linear range 6.0–40.0 ng for ASA with coefficient of determination R_2 = 0.99. The LOD and LOQ values were 0.9 and 3.0 ng for ASA, respectively. The repeatability of developed method was evaluated as relative standard deviation (RSD% = 2.7). The proposed method was also used to determine ASA in human plasma and serum as biological samples, which recovery results were within 89.0–100.0%.

Keywords
Nanocomposite; Dispersive magnetic solid phase extraction; Aspirin; Ion mobility spectrometry; Biological samples

1.INTRODUCTION

Aspirin (ASA) is an important compound which is used as an anti-inflammatory, anti-pyretic and analgesic drug for its effectiveness in the treatment of many diseases such as coronary heart, cancer, preeclampsia, headache, alzheimer, cardiovascular [1–3]. Based on the pharmacological studies, ASA is hydrolyzed to salicylic acid in human body and this acid is the responsible of ASA activity. It is toxic at higher amounts of 2.2 mM so that the incorrect ASA dose can damage to stomach wall and lead to stomach ulcers [4, 5]. Therefore, according to above matters (high consumption and the overdose hazards) the ASA analysis is important. Different analytical methods have been reported by researchers for this purpose [6–10].

Dispersive magnetic solid phase extraction (DMSPE) is a novel approach of SPE which has been considerably used in sample preparation field. In this technique, the dispersive magnetic nanoparticle (MNP) adsorbents in the sample solution are gathered simply by using a magnet [11, 12].

The compounds containing Fe, Co or Ni [11] are used as MNPs which among them Fe_3O_4 is the most commonly interested due to simple preparation, bioapplications, wastewater treatments, excellent paramagnetic properties, low toxic and cost [13, 14]. On the other hand, Fe_3O_4 particles easily accumulate in the aqueous samples that this can reduce their surface areas and resulting adsorption efficiency [15, 16]. Moreover, the oxidation reaction of the Fe_3O_4 naked NPs leads to a phase change [17]. Fe_3O_4 NPs combined with other metal oxides has been employed to eliminate or reduce of these limitations [11]. The Peng research team combined $Cu(OH)_2$ to Fe_3O_4 NPs by coprecipitation procedure, so that the nanocomposite presented the better results than Fe_3O_4 alone [18].

Nanocarbon compounds were widely utilized as efficient adsorbents in SPE techniques because of properties such as their high surface area, and appropriate physical and chemical structures [19]. Among, graphene was a key and remarkable compound due to its unique properties [20]. Graphene was converted to graphene oxide (GO) via an oxidation reaction that this could be improved its hydrophilic properties and applications in water samples [21]. GO has also been combined with magnetic nanoparticles and used widely as a promising adsorbent in DMSPE studies [22].

Ion mobility spectrometry (IMS) is an analytical technique for the detection and determination of trace analytes. In IMS, the chemical compounds (gaseous ions) are separated based on their ionic

* Corresponding author:
sheibani@iauyazd.ac.ir or alisheibani@ymail.com

mobility in a weak electric field (drift tube) and atmospheric pressure. During drift tube, the analyte ions are separated based on their size, shape, mass, and charge at a range of drift times. The total numbers of ions are calculated for quantitative assay. IMS is applied to detect a wide ranging of compounds such as drugs, pollutants, and explosives. The simplicity, low cost, short analysis time, and high sensitivity are the main advantages of IMS methods [23–26].

In this work, DMSPE technique was developed to extraction and preconcentration of ASA. Combining GO with Fe_3O_4 NPs and also CuO was performed for improving the adsorption performance of adsorbent. IMS method equipped with a corona discharge source was used to determine ASA.

The effective parameters of DMSPE–IMS (extraction and determination) were investigated and optimized. The proposed method was certified and also its capability was successfully evaluated and confirmed in the ASA analysis of biological samples.

2.EXPERIMENTAL

2.1. Materials

ASA tablets (80 mg) were obtained from Pharma Chemie Co (Iran). The stock solutions (100 µg/mL) were prepared in methanol. Iron (III) chloride ($FeCl_3$), iron (II) sulfate ($FeSO_4$), copper (II) chloride ($CuCl_2$), sodium hydroxide (NaOH), and ethanol were purchased from Merck Co.

2.2. Instrumentation

In this research, an ion mobility spectrometer (IMS−400, TOF Tech. Pars Company, Iran) equipped to continuous corona discharge as an ionization source was used. A full description of the IMS instrumentation was seen in Ref. [26]. The total peak area (from first to final peaks) of analyte was integrated and considered as IMS response. The operational conditions of IMS were investigated.

2.3. The adsorbent preparation (Fe_3O_4@CuO&GO)

GO was synthesized by Hummers procedure with a minor change [27]. Fe_3O_4@CuO&GO nanocomposite was prepared via a modified precipitation method in a N_2 atmosphere. The mass ratio of 9% GO to 91% Fe and Cu was found the optimal value for the preparation of nanocomposite.

Fe_3O_4@CuO&GO was prepared as follows: GO was added to deionized water and mixed by ultrasonic vibration for 2 h. Then, the solutions of $FeCl_3$ (0.1 M), $FeSO_4$ (0.2 M) and NaOH (1.5 M) simultaneously and gradually were add into the reactor vessel. The mixture was stirred for 1 h, and then; the $CuCl_2$ (0.1 M) and NaOH (1.5 M) solutions were simultaneously poured into the reactor and it was mixed for 1 h. After, the created precipitation was separated and washed continuously with deionized water and ethanol and then, freezing in half a day. Finally, solid products were crushed, sieved and kept in a desiccator before SPE [28].

2.4. DMSPE and IMS analysis

40 mg of adsorbent (Fe_3O_4@CuO&GO nanocomposite) was washed with 5 mL of methanol and deionized water, respectively. It was added to an aqueous solution containing 10 ng/µL of ASA at pH 8 and a homogenous suspension was established. The solution was mixed in a laboratory beaker for 10 min and the dispersive adsorbents were collected using an external magnet. The drugs adsorbed on the nanocomposite materials were desorbed by 1 mL methanol (desorption solvent) and also it was shaken in an ultrasonic bath for 3 min. The extract liquid (1 µL) was injected into the IMS for drug analysis.

2.5. The real sample preparation

The drug–free human plasma and serum samples were obtained from Pars Laboratory (Yazd, Iran). These samples were spiked with the standard solution of ASA in linear range of 6.0–40.0 ng. The spiked plasma sample (1 mL) was mixed with methanol (1 mL) to protein precipitation. Then, the solution was vortexed and centrifuged at 4000 rpm for 6 min, and the supernatant was diluted with water (1:3, v/v). The pH of solution was adjusted by adding the dilute solutions of HCl or NaOH and then, the plasma sample was treated by SPE for the clean up and extraction [29].

To prepare serum sample, 100 µL of the spiked sample was mixed well with 900 µL of methanol and followed by centrifugation for 10 min at 4000 rpm. The supernatant of the sample solution was taken and diluted with 3 mL of deionized water. Finally, the serum sample was treated by SPE for the clean up and extraction [30]..

3.RESULTS AND DISCUSSION

3.1. Characterization of Fe_3O_4@CuO&GO

X–ray diffraction (XRD) technique confirmed the crystalline structure of the produced nanocomposite adsorbent. The XRD pattern of Fe_3O_4@CuO&GO is shown in Fig 1. The diffraction peaks at 2θ values: 30.1°, 35.6°, 43.1°, 53.9°, 57.0°, 62.7° corresponded to diffraction planes in (220), (311), (400), (422), (551) and (440), respectively (JCPDS card no. 19-0629) [31]. According to XRD pattern, the core of Fe_3O_4 nanoparticles did not change during anchoring onto the surface of GO and also CuO peaks were not appeared due to their high dispersion [32].

DOI: 10.30473/ijac.2023.67944.1269

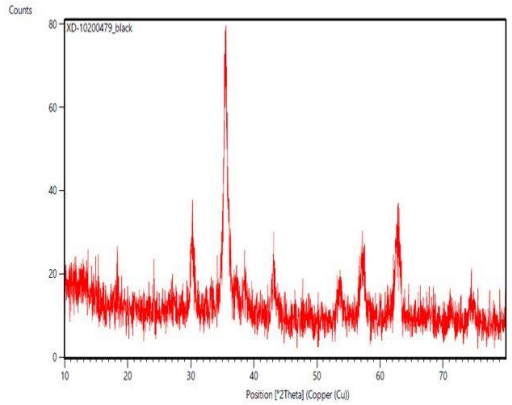

Fig 1. XRD pattern of Fe_3O_4@CuO&GO.

The surface morphology of nanocomposite adsorbent was studied by using scanning electron microscopy (SEM). The SEM image of Fe_3O_4@CuO&GO is displayed in Fig 2. Adsorbent showed a flake–like structure in which CuO and Fe_3O_4 nanoparticles were distributed homogeneously all over the surface of GO. According to Fig 2, CuO and Fe_3O_4 were appeared as the dark or lighter color points on the GO surfaces [33].

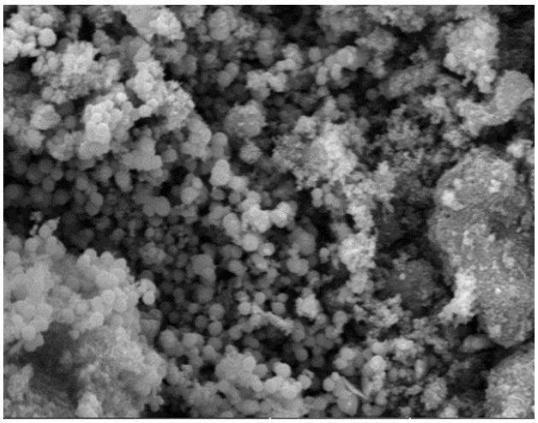

Fig 2. SEM image of Fe_3O_4@CuO&GO.

The FT–IR analysis of Fe_3O_4@Cu&GO, before and after adsorption process; were also followed. According to Fig 3, the absorption bands at 3420 cm-1 and 1126 cm-1 were attributed to stretching modes of O-H and C-O groups, respectively [34]. The peak at 1625 cm-1 can be assigned to the skeletal vibrations of graphitic domains of GO. The presence of Fe3O4/CuO in adsorbent structure was proved due to absorption band at 566 cm-1 [35]. Based on Fig. 3, the absorption band in 1625 cm-1 has been shifted to 1636 cm-1. Regard to this change and also the molecular structures of drug and adsorbent, the mechanism of sorption can be associated to interactions between the oxygen and nitrogen groups and also π–π interactions the aromatic parts (C=C groups) of ASA with adsorbent.

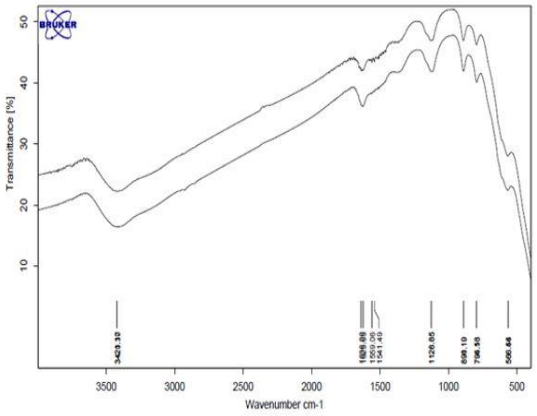

Fig 3. FT−IR spectra of Fe_3O_4@CuO&GO, before (down) and after (top) ASA adsorption.

3.2. IMS operating conditions

The ion mobility spectrum of ASA illustrated a peak in 8.4 ms (Fig 4). It was completely separate and far from the reactant ion and background peaks (4.5-6.7 ms). Effective instrumental parameters including corona and drift voltages, injection and tube (cell) temperatures, carrier and drift gas flow rates and also pulse width were investigated and optimized. The IMS operating conditions for the determination of drug are reported in Table 1.

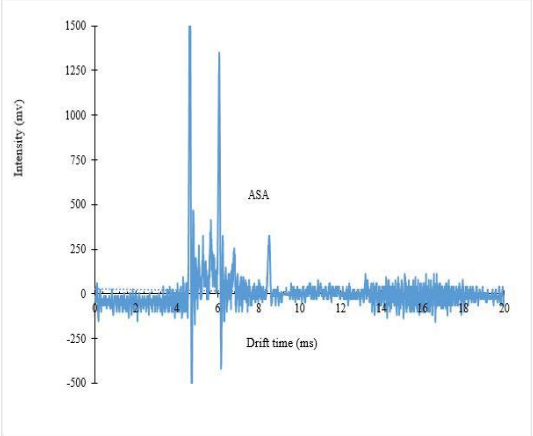

Fig 4. Ion mobility spectrum of ASA.

Table 1. The operational conditions of IMS for the determination of ASA.

Parameter	Setting
Corona voltage	2300 V
Drift voltage	7000 V
Injector port temperature (170-230 ºC)	190 °C
IMS cell temperature (150-200 ºC)	170 °C
Flow of drift gas (N_2, mL min^{-1})	600
Flow of carrier gas (N_2, mL min^{-1})	300
Shutter grid pulse width	100 μs
Corona discharge mode	Positive

DOI: 10.30473/ijac.2023.67944.1269

3.3. DMSPE optimization

In order to reach the suitable extraction and preconcentration using the proposed DMSPE, the experimental parameters affecting the recovery including desorption solvent, pH, adsorbent amount, extraction time and temperature must be investigated and optimized.

3.3.1. Desorption solvent

In this work, desorption solvent is an important factor that it was studied by using common organic solvents including acetonitrile, methanol, dichloromethane/acetonitrile,
acetonitrile/methanol. The best IMS response was acquired with acetonitrile or methanol. But, since methanol is a compatible solvent for the IMS analysis, it was selected as the proper desorption solvent (1 mL) for the present study.

3.3.2. pH

As shown in Fig 5, at low and high pH values; the ASA extraction did not lead to good results. In most of the extraction studies of ASA by Fe-containing oxide adsorbent, the low recovery results were obtained with increasing PH. This can be related probability to compete OH^- and ASA for capturing the active sites of adsorbents [36]. Also, in acidic medium; the low recovery results observed may be due to protonate the oxygen atoms of ASA. Therefore, pH=8 was chosen as optimum value.

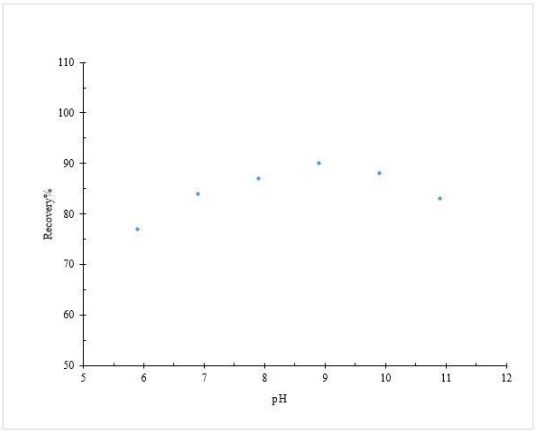

Fig 5. Effect of pH on recovery%. Conditions: ASA: 10 ng, desorption solvent (methanol): 1 mL, amount of adsorbent: 40 mg, extraction time: 10 min, extraction temperature: 25 ºC, analyte solution volume: 20 mL.

3.3.3. The amount of adsorbent

The amount of Fe_3O_4@CuO&GO adsorbent has an impact considerably on the extraction efficiency. To check this parameter, a series of experiments in range 15 to 50 mg of adsorbent was done (Fig 6). According to this Fig, the ASA adsorption was improved by increasing the amount of adsorbent until 40 mg and then, the recovery results were constant. Therefore, 40 mg of Fe_3O_4@CuO&GO was used for future tests.

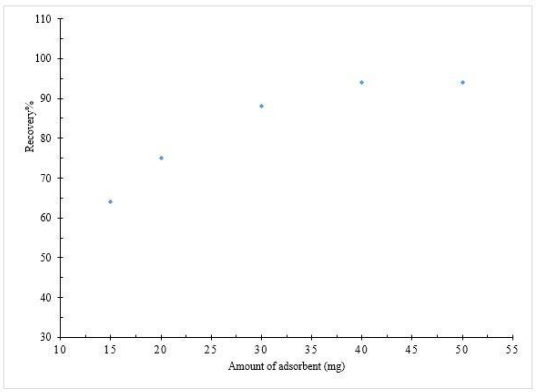

Fig 6. Effect of adsorbent amount on recovery%. Conditions: ASA: 10 ng/µL, desorption solvent (methanol): 1 mL, PH = 9, extraction time: 10 min, extraction temperature: 25 ºC, analyte solution volume: 20 mL.

3.3.4. Extraction time

In DMSPE technique, the extraction (adsorption) time is an important parameter. The effect of this parameter was investigated over a period range of 5 to 20 min. According to Fig 7, the extract of ASA has been completed in 10 min and then, adsorption recovery was lowered. This trend can be justified due to compete between adsorption and desorption processes. Hence, 10 min was a suitable time for adsorption process.

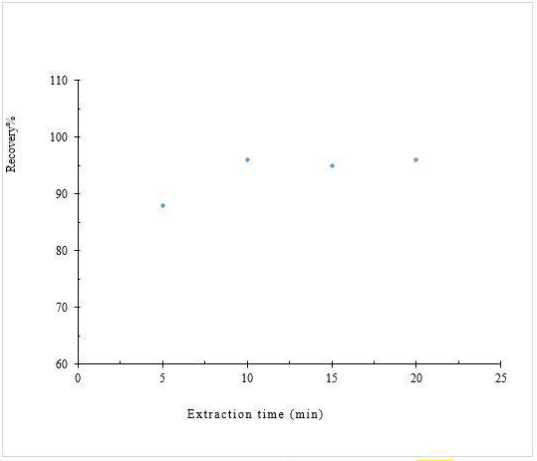

Fig 7. Effect of extraction time on recovery%. Conditions: ASA: 10 ng/µL, desorption solvent (methanol): 1 mL, pH = 9, amount of adsorbent: 40 mg, extraction temperature: 25 ºC, analyte solution volume: 20 mL.

3.3.5. Extraction temperature

The effect of temperature on the extraction recovery was investigated in range of 20 to 40 ºC. Fig 8 shows that the adsorption recovery is increased with increasing temperature up to 25 ºC. At the higher temperature of 30 ºC, the extraction

DOI: 10.30473/ijac.2023.67944.1269

recovery was reduced due to desorption process. Therefore, 25 ºC was selected as a suitable temperature for the developed DMSPE in this work.

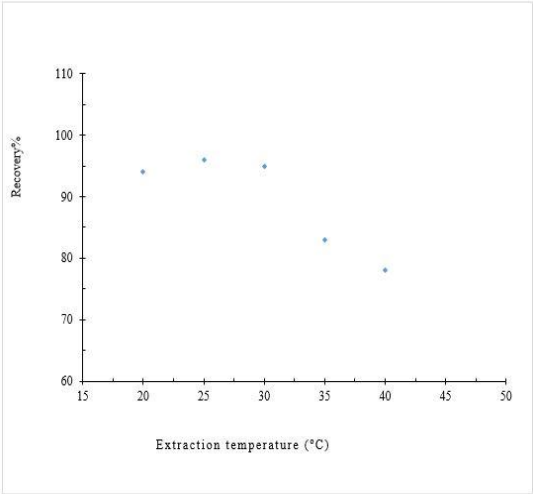

Fig 8. Effect of extraction temperature on recovery%. Conditions: ASA: 10 ng/µL, desorption solvent (methanol): 1 mL, amount of adsorbent: 40 mg, pH = 9, extraction time: 10 min, analyte solution volume: 20 mL.

3.4. Method validation

For evaluating the developed DMSPE–IMS method, parameters including linear dynamic range (LDR), determination coefficient (R_2), detection limit (LOD), quantitative limit (LOQ) and repeatability or precision (RSD) were calculated. The results are reported in Table 2. The calibration curve of ASA was linear in the ranging of 6.0–40.0 ng with the coefficient of determination 0.998. The LOD and LOQ values of developed method were determined using 3Sb/m and 10 Sb/m equations, respectively; where Sb was the standard deviation of blank signal and m was the slope of calibration curve. These values were 0.9 and 3.0 ng for ASA, respectively. The repeatability of proposed method was also valued that was 2.7%. The enrichment factor (EF) 20 can be claimed for the presented DMSPE system. Fe_3O_4@CuO&GO nanosorbent was reused by five successive adsorption–desorption cycles using methanol as desorption solvent.

Table 2. The Analytical parameters of the proposed DMSPE-IMS method for the determination of ASA.

Parameter	ASA
LDR (ng)	6.0–40.0
R^2	0.99
LOD (ng)	0.9
LOQ (ng)	3.0
RSD%	2.7
Recovery%	97.0

3.5. Method bioapplication

In order to assign the capability and bioapplication of the proposed method, the recovery examinations were done by adding different amounts from ASA (regard to LDR) to the real samples (plasma and serum). The analyte was extracted by the developed DMSPE technique described in the experimental section and then, the extracted drug was injected into the IMS. The recovery results reported in Table 3 (within 89.0–100.0%) proved the capability of the developed DMSPE–IMS method to quantitatively detect ASA in biological samples. In Table 4, the analytical parameters of the proposed method have been compared to those of other methods used for the determination of ASA drug. The proposed method presented superior precision with respect to several other methods [7, 16]. The LDR was also better or comparable with the mentioned methods.

Table 3. The recovery results of ASA from biological samples using the proposed DMSPE-IMS method.

Sample	Added (ng)	Recovery%
Plasma	6.0	94.0
	8.0	91.0
	10.0	96.0
	12.0	95.0
	14.0	95.0
	16.0	93.0
	20.0	97.0
Serum	6.0	89.0
	8.0	92.0
	10.0	99.0
	12.0	90.0
	14.0	89.0
	16.0	94.0
	20.0	100

4.CONCLUSION

In this work, off–line coupling a magnetic Fe_3O_4@Cu&GO nanocomposite as an adsorbent for DMSPE technique and IMS method were developed to extraction and determine ASA. The proposed method offered advantages such as low amount of adsorbent, low organic solvent consumption, good LOD (0.9 ng) and LOQ (3.0 ng) values, relative wide LDR (6.0-40.0 ng) and acceptable recovery (97.0%). Furthermore, the proposed method was successfully exploited to determine ASA in human plasma and serum as biological samples, which recovery results were within 89.0–100.0%.

DOI: 10.30473/ijac.2023.67944.1269

Table 4. Comparison of the proposed IMS method with the other methods for the extraction and determination ASA.

Determination method	Sample	Sample preparation	LDR (ng/mL)	LOD (ng/mL)	LOQ (ng/mL)	RSD (%)	Recovery (%)	Ref
Voltammetric	Tablet	Poly(diaquabis(1,10-phenanthroline)Copper(II)chloride) modified glassy carbon electrode	180-3600	7.02	23.4	3.7	96.5-100.5	7
RP-HPLC	Tablet	Thermo Scientific Hypersil ODS column	$(1\text{-}150)\times10^{3}$	69	230	-	98.0-102.0	8
Electrochemical	Urine, Saliva and Pharmaceutical tablet	An electrochemical sensor based on Chitosan capped with Gold nanoparticles	(0.001-1000)	0.03×10^{-3}	_	2.0	90.0-98.0	6
LC-MS	Pharmaceutical	Crushed knotweed (Fallopia x bohemica) leaves as a biosorbent	-	500	1000	-	17.3 (mg/g, capacity)	9
HPLC-UV	Urine/Plasma	Banana peel/Silicon glue coated stir bar	(0.2–200)	(0.04–0.5)	(0.15–1.65)	4.9	94.0<	10
DMSPE-IMS	Serum /Plasma	Fe_3O_4@CuO&GO	$(6.0\text{-}40.0)\times10^{3}$	9.0×10^{2}	3.0×10^{3}	2.7	(89.0-103.0)	This work

Acknowledgements

This work was financially supported by Yazd Branch, Islamic Azad University (IAU), Yazd, Iran.

REFERENCES

[1]R. H. Böger, S. M. Bode-Böger, F. M. Gutzki, D. Tsikas, H. P. Weskott, and J. C. frölich, Rapid and selective inhibition of platelet aggregation and thromboxane formation by intravenous low dose aspirin in man, *Clin. Sci.* 84 (1993) 517-524.

[2]S. Weggen, M. Rogers, and J. Eriksen, NSAIDs: small molecules for prevention of Alzheimer's disease or precursors for future drug development, Trends Pharmacol, *Sci* 28 (2007) 536-543.

[3]T. S. Poulsen, S. R. Kristensen, L. Korsholm, T. Haghfelt, B. Jørgensen, P. B. Licht, and H. Mickley, Variation and importance of aspirin resistance in patients with known cardiovascular disease, *Thromb. Res.* 120 (2007) 477-484.

[4]A. L. Sun, Y. Q. Cai, R. Yuan, and G. F. Gui, Highly Selective Salicylate Membrane Electrode Based on N, N′-(Aminoethyl) ethylenediamide Bis (2-salicylideneimine) Binuclear Copper (II) Complex as Neutral Carrier, *Chin. J. Chem.* 24 (2006) 894-898.

[5]T. J. Moore, M. J. Joseph, B. W. Allen, and L. A. Coury, Enzymically amplified voltammetric sensor for microliter sample volumes of salicylate, *Anal. Chem.* 67 (1995) 1896-1902.

[6]A. Diouf, M. Moufid, D. Bouyahya, L. Österlund, N. El Bari, and B. Bouchikhi, An electrochemical sensor based on chitosan capped with gold nanoparticles combined with a voltammetric electronic tongue for quantitative aspirin detection in human physiological fluids and tablets, *Mater. Sci. Eng: C.* 110 (2020) 110665.

[7]A. Mebrie, M. Amare, A. Kassa, Y. B. Yohannes, A. Tesfaye, A. Abebe, and T. Asmelash, Novel poly (diaquabis (1, 10-phenanthroline) copper (II) chloride) modified glassy carbon electrode for square wave voltammetric determination of aspirin in tablet samples, *Sens. Int.* 3 (2022) 100187.

[8]A. H. Kamal, A. A. Marie, and S. F. Hammad, Stability indicating RP-HPLC method for simultaneous determination of omeprazole and aspirin in the presence of salicylic acid as degradation product, *Microchem, J.* 152 (2020) 104350.

[9]M. Mucha, and M. Mucha, Ibuprofen and acetylsalicylic acid biosorption on the leaves of the knotweed Fallopia x bohemica, *New J. Chem.* 41 (2017) 7953-7959.

[10]Z. Jafari, and M. R. Hadjmohammadi, A banana peel/silicon glue coated stir bar for extraction of aspirin, diclofenac, ibuprofen and mefenamic acid followed by high performance liquid chromatography-UV detection, *Anal. Methods.* 12 (2020) 4429-4437.

[11]K. K. Kefeni, B. B. Mamba, and T. A. Msagati, Application of spinel ferrite nanoparticles in water and wastewater treatment: a review, *Sep. Purif. Technol.* 188 (2017) 399-422.

[12]J. Gamonchuang, Y. Santaladchaiyakit, and R. Burakham, Magnetic Solid-Phase Extraction of Carbamate Pesticides Using Magnetic Metal–Organic Frameworks Derived from Benzoate Ligands, Followed by Digital Image Colorimetric Screening and High-Performance Liquid Chromatography Analysis, *ACS Omega.* 7 (2022) 12202-12211.

[13]J. Gómez-Pastora, E. Bringas, and I. Ortiz, Recent progress and future challenges on the use of high performance magnetic nano-adsorbents in environmental applications, *Chem. Eng. J.* 256 (2014) 187-204.

[14]J. Gómez-Pastora, S. Dominguez, E. Bringas, M. J. Rivero, I. Ortiz, and D. D. Dionysiou, Review and perspectives on the use of magnetic nanophotocatalysts (MNPCs) in water treatment, *Chem. Eng. J.* 310 (2017) 407-427.

[15]M. Lima, D. Macuvele, L. Muller, J. Nones, L. Silva, M. Fiori, C. Soares, and H. Riella, Synthesis and potential adsorption of Fe_3O_4@ C core-shell nanoparticles for to removal of pollutants in aqueous solutions: a brief review, *J. Adv. Chem. Eng.* 7 (2017) 1-11.

[16]K. Kalantari, M. B. Ahmad, K. Shameli, M. Z. B. Hussein, R. Khandanlou, and H. Khanehzaei, Size-controlled synthesis of Fe_3O_4 magnetic nanoparticles in the layers of montmorillonite, *J. Nanomater.* 14 (2014) 181-181.

[17]L. Chen, C.H. Zhou, S. Fiore, D. S. Tong, H. Zhang, C. S. Li, S. F. Ji, and W. H. Yu, Functional magnetic nanoparticle/clay mineral nanocomposites: preparation, magnetism and versatile applications, *Appl. Clay Sci.* 127 (2016) 143-163.

[18]B. Peng, T. Song, T. Wang, L. Chai, W. Yang, X. Li, C. Li, and H. Wang, Facile synthesis of Fe_3O_4@ $Cu(OH)_2$ composites and their arsenic adsorption application, *Chem. Eng. J.* 299 (2016) 15-22.

[19]C. Cha, S. R. Shin, N. Annabi, M. R. Dokmeci, and A. Khademhosseini, Carbon-based nanomaterials: multifunctional materials for biomedical engineering, *ACS nano.* 7 (2013) 2891-2897.

[20]R. Sitko, B. Zawisza, and E. Malicka, Graphene as a new sorbent in analytical chemistry, *TrAC, Trends Anal. Chem.* 51 (2013) 33-43.

[21]X. Chen, Z. Qu, Z. Liu, and G. Ren, Mechanism of Oxidization of Graphite to Graphene Oxide by the Hummers Method, *ACS Omega.* 7 (2022) 23503-23510.

[22]M. J. Santoyo Treviño, S. Zarazúa, and J. Płotka-Wasylka, Nanosorbents as Materials for Extraction Processes of Environmental Contaminants and Others, *Molecules* 27 (2022) 1067.

[23]Y. Valadbeigi, V. Ilbeigi, A. Afgar, and M. Soleimani, Comparison of the positive and negative modes of corona discharge ion source for direct determination of aspirin in urine by ion mobility spectrometry, *Int. J. Mass Spectrom.* 470 (2021) 116699.

[24]M. R. Shishehbore, S. J. Aghili, and A. Sheibani, On-line Coupling of Dynamic Headspace Extraction and Ion Mobility Spectrometry for Evaluating Oxidation in Sesame Oil, *Iran. J. Anal. Chem.* 6 (2019) 33-38.

[25]M. T. Jafari, B. Rezaei, and H. Bahrami, Zirconium dioxide-reduced graphene oxide nanocomposite-coated stir-bar sorptive extraction coupled with ion mobility spectrometry for determining ethion, *Talanta* 182 (2018) 285-291.

[26]T. Keller, A. Keller, E. Tutsch-Bauer, and F. Monticelli, Application of ion mobility spectrometry in cases of forensic interest, *Forensic Sci. Int.* 161 (2006) 130-140.

[27]W. S. Hummers, and R. E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (1958) 1339-1339.

[28]K. Wu, C. Jing, J. Zhang, T. Liu, S. Yang, and W. Wang, Magnetic Fe_3O_4@ CuO nanocomposite assembled on graphene oxide sheets for the enhanced removal of arsenic (III/V) from water, *Appl. Surf. Sci.* 466 (2019) 746-756.

[29]M. Safari, M. Shahlaei, Y. Yamini, M. Shakorian, and E. Arkan, Magnetic framework composite as sorbent for magnetic solid phase extraction coupled with high performance liquid chromatography for simultaneous extraction and determination of tricyclic antidepressants, *Anal. Chim. Acta.* 1034 (2018) 204-213.

[30]T. M. Alshammari, A. A. Al-Hassan, and T. B. Hadda, M. Aljofan, Comparison of different serum sample extraction methods and their suitability for mass spectrometry analysis, Saudi Pharm, *J.* 23 (2015) 689-697.

[31]S. Liu, Q. Xu, S. S. Latthe, A. B. Gurav, and R. Xing, Superhydrophobic/superoleophilic magnetic polyurethane sponge for oil/water separation, *RSC Adv.* 5 (2015) 68293-68298.

[32]Y. Jain, M. Kumari, R. P. Singh, D. Kumar, and R. Gupta, Sonochemical decoration of graphene oxide with magnetic Fe_3O_4@CuO nanocomposite for efficient click synthesis of coumarin-sugar based bioconjugates and their cytotoxic activity, *Catal. Lett.* 150 (2020) 1142-1154.

[33]A. Q. Alorabi, M. S. Hassan, and M. Azizi, Fe_3O_4-CuO-activated carbon composite as an efficient adsorbent for bromophenol blue dye removal from aqueous solutions, *Arabian J. Chem.* 13 (2020) 8080-8091.

[34]S. Stankovich, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets, *Carbon* 44 (2006) 3342-3347.

[35]M. Kidwai, V. Bansal, N. K. Mishra, and A. Kumar, S. Mozumdar, Copper-nanoparticle-catalyzed A_3 coupling via CH activation, *Synlett* 7 (2007) 1581-1584.

DOI: 10.30473/ijac.2023.67944.1269

[36]B. Shao, Y. Guan, Z. Tian, X. Guan, and D. Wu, Advantages of aeration in arsenic removal and arsenite oxidation by structural Fe(II) hydroxides in aqueous solution, *Colloids Surf. A.* 506 (2016) 703-710.

DOI: 10.30473/ijac.2023.67944.1269

کاربرد بیولوژیکی استخراج فاز جامد پخشی مغناطیسی با استفاده از نانوکامپوزیت Fe_3O_4@Cuo&GO و طیف سنجی تحرک یونی: تعیین آسپرین

فریده شمسی، علی شیبانی*، مسعود رضا شیشه بر

.ایران یزد، اسلامی، آزاد دانشگاه شیمی، واحد یزد، گروه
* E-mail: sheibani@iauyazd.ac.ir / alisheibani@ymail.com

تاریخ دریافت: ۲۶ اردیبهشت ۱۴۰۲ **تاریخ پذیرش:** ۴ تیر ۱۴۰۲

چکیده

در این مطالعه، تکنیک استخراج فاز جامد پخشی مغناطیسی با استفاده از ترکیب گرافن اکسید با مگنتیت و مس اکسید(Fe_3O_4@CuO&GO) برای استخراج آسپرین از نمونه‌های بیولوژیکی توصیف شده است. مورفولوژی و ساختار نانوکامپوزیت با استفاده از تکنیک‌های XRD، SEM و FTIR مشخص و آنالیز شد. طیف¬سنجی تحرک یونی مجهز به منبع یونیزاسیون تخلیه کرونا برای تعیین آسپرین مورد بهره برداری قرار گرفت. پارامترهای استخراج (حلال واجذبی، PH، مقدار جاذب، زمان استخراج و دما) و همچنین پارامترهای عملکردی طیف¬سنجی بررسی و بهینه شدند. تحت شرایط بهینه، روش پیشنهادی در محدوده خطی ۶ تا ۴۰ نانوگرم برای آسپرین با ضریب تعیین R_2 = 0.99 خطی بود. مقادیر حد تشخیص و حد تعیین برای آسپرین به ترتیب ۰,۹ و ۳ نانوگرم حاصل شد. تکرارپذیری روش توسعه یافته به صورت انحراف استاندارد نسبی (RSD% = 2.7) ارزیابی و گزارش شد. روش پیشنهادی برای تعیین آسپرین در پلاسما و سرم به عنوان نمونه‌های بیولوژیکی بکار گرفته شد که نتایج بازیابی بین ۸۹ تا ۱۰۰ درصد شد.

کلید واژه ها

نانوکامپوزیت؛مغناطیسی ؛استخراج فاز جامد پخشی مغناطیسی ؛ آسپرین؛ طیف¬سنجی تحرک یونی ؛ نمونه¬های بیولوژیکی