

Determination of Methamphetamine by GC-Mass based on Molecularly Imprinted Solid-phase Used 2-hydroxy Ethyl Methacrylate as Functional Monomer

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Abstract: A novel method characterized by high sensitivity, low cost and high stability was developed. This method based on a molecularly imprinted polymer (MIP) using a functional monomer which is 2-vinylpyridine (2-VP) and 2-hydroxyethyl methacrylate (2-HEMA), suitable cross-linker and the template which is MAMP to fabricate a monolithic solid-phase micro extraction (SPME) fiber. A polymer was also prepared without selective binding sites this was referred to as a non-imprinted polymer (NIP). (SPME) with gas chromatography and mass spectrometry (GC/MS); all these analytical methods used to extraction, pre-concentration and selective determination of methamphetamine (MAMP) and its derivatives. Firmness, stability and duration of the fabricated fiber give it its fundamental and indispensable role in SPME. The samples were collected from methamphetamine suspected abuser donate provided from the medico legal Directorate (Baghdad, Iraq). Monitoring of the analytes was performed using a (GC MS) and using UV-vis and Scanning electron microscopy (SEM) and FTIR. The relative standard deviations (RSD%) for five Patients repeated experiments for three measurements are range of (at 30-60 ppm of MAMP) is (1.20-3.61) %. The relative recoveries obtained for MAMP in spiked human urine samples are in the range of (93.63-99.71).

Keywords: Methamphetamines/Molecularly imprinted polymer / GC / MS.

INTRODUCTION

Methamphetamine (MAMP) is one of the stimulants of the central nervous system. These drugs affect orgasm and hallucinations and enhance the ability to stay awake [1]. The powerful potential of the drug is addictive and addictive, as is the effect of toxicity tolerance on users. Because of the widespread use of this drug, this clinical lead and forensic laboratory routinely conducts some tests on MAMP and its metabolites. Typically, samples must be processed through one of the following methods: liquid fluid extraction (LLE) and solid phase extraction (SPE) [2-6]. Because of time and organic solvents that are heavily used to adjust and remove the sample, this multi-step procedure results in the analyst being wasted. Precision extraction at SPME is easy, strong, and fast. This method does not require any solvent. These characteristics solve many difficulties in sampling and sample injection into an analytical device. The newly developed method, such as direct SPME [7, 8], headspace SPME [9-12] and SPME [13] were used in the tube to determine MAMP.

There is a real need to get rid of the least selectivity which is a major drawback of this method which leads to significant obstacles in sample analysis. On the other hand, commercially available fibers are characterized by low stability, low selectivity, not strong enough and very expensive, so there is a need to improve the properties of these fibers. [14-17]. MIP is based on the use of materials with high-ability properties to identify specifically the analytical molecules that make up the identification sites specified in the polymer matrix by structure in an analytical presence such as particle printing. Through the use of

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a common polymerization process for monomer, we can obtain cross-linked synthetic polymers, which are performed in the presence of a template molecule. Both the polymer and the mold are washed, and contain specific sites that are recognized as sites of recognition. These sites and model particles complement each other in shape, size and chemical function. MIP shows the ability to selectively select the template and its derivatives which was applied for determine several drugs as ibuprofen[18], warfarin[19] and Mebeverine Hydrochloride [20].

The aim of this study is to identify methamphetamine (MAMP) by preparing new MIPs that are used as solid-phase recovery and mass-spectrometry (GC-MS) as a detector.

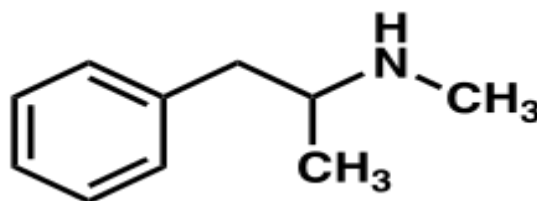


Fig.1: Structure of methamphetamine (MAMP)

Experimental Reagents and Chemicals

2-Vinyl pyridine (2-VP), (2-hydroxy ethyl methacrylate)(2-HEM),divinyl benzene (DVB), Trimethylpropane trimethacrylate (TMPTMA)and benzoyl peroxide were purchased from Sigma–Aldrich (St. Louis, MO, USA, www.sigma-aldrich.com), methanol, chloroform, acetonitrile, acetic acid, formic acid and trifluoroacetic (TFA)anhydride were purchased from Merck (Darmstadt, Germany, www.merck.com.) Methamphetamine (MAMP) was provided from the medico legal institution (Baghdad, Iraq).nitrogen gas (99.99) from Arab gulf factory Baghdad.

Instrumentation

The control was performed using GC MC (Ategentl chnologies (7890A) (United States of America) and the use of UV (Shimadzu uv spectrophotometer 1800 pc) and scanning electron microscopy (SEM) (JSM.6390A). FTIR Shimadzu (FTIR) - 8000 (Japan), heating / series. Chromatography is the separation of a mixture of compounds mixed into monoclonal components and then estimated by following three steps using GC.

1. Injecting a sample into the GC.
2. Separate the sample into individual components.
3. Detection of compounds in the sample.

During this process, status messages are displayed from Agilent 7890A GC, and user changes can be made to parameter settings through the operator panel. Ultraviolet radiation was used to measure pure methamphetamine uptake of 258 nm and was then used again to measure MIP-methamphetamine uptake, which was pre-washed after washing to ensure that all methamphetamine was removed. Sonerx (W.GERMANY) was used to stir up the prepolymer solution.

MIP procedure

2.0 mmol template (MAMP) was dissolved in 20 mL porogen (acetonitrile) and 2 mmol of functional monomer 2-Vinyl pyridine (2-VP) was added. After the ultrasonic flipping, the resulting mixture was added for 10 minutes, 10.5 mmol via the DVB link and 10 mg initiator (benzoyl peroxide) to the solution. The solution was bubbled with nitrogen for 15 min and used as bulk solution. Sealed the tub by the rubber. Then the tub was leaved in the water bath at 55c overnight. After completion of the polymerization, the wire was completely withdrawn.

The coating was performed with a NIP layer in the same manner as described above except that MAMP was not included in the polymerization process.MIP and NIP coated tubes were washed several times with an excess amount of nitric acid / acetic acid / distilled water multiplier (30:5:15, v / v / v) in the ssucsulait for 48 hours until Remove the mold and the non-reacting compounds as much as possible and dry them for 2 hour in a vacuum. MIP and NIP were prepared in the oven to examine MIP and NIP prepared in the oven for its dosage. Before extraction, from the sampling device and used as extraction needles.

Daring. Before extraction, from the sampling device and use it as extraction wells. The plastic injector (Colum) was filled with the MIP using a plastic syringe.

The solution (urine or standard solution) was poured from the top end of the Colombian. The solution movement was at an electric discharge at 70 rpm.

Sampling Procedure

Prepare a stock solution at concentration (30, 60, 90, 120, 150 ppm) of MAMP at pH 8 passed through Colum at a flow rate of 70 rpm. The colum was washed twice with 2 mL distilled water to remove the matrix interference and then removed from the MIP.

The Sampling Device

A 3 ml plastic syringe was used and each syringe was filled with different weights ranging (0.2, 0.4, 0.6 gm) from MIP which was previously grinded and sifted (0.75 microns).

Real Sample

Urine samples of suspected methamphetamine were collected and sent at the request of the judge to forensic medicine (Bagda, Iraq). The centrifuge sample was at 5000 rpm for 10 minutes to get rid of any precipitated material. The urine supernatant was directly impregnated with methamphetamine, and the non-pointed and squid samples were subjected to extraction by Colom.

Extraction Procedure

Methamphetamine was extracted from urine using MIP methamphetamine solid phase extraction (SPE) column. This Colum was prepared by packing it with a machete, 0.4 gm, the size of its container, 3 ml. The SPE vacuum was loaded with floating material from the urine sample centrifuged at a flow rate (70 rpm). 1 mL of distilled water was then added 1 ml of acetonitrile / distilled (70:30, v / v) to the Colum. After the light of the ceiling was collected from Colum in the small beaker. Then it was dried for 10 minutes. 1 ml of acetic acid / acetonitrile (1: 100, v / v) was added and the plates were also collected in the same cup and dried again in a water bath at 50c. To the remaining in the beaker; 2 ml of Formic Acid Methanol (1: 100, v / v) was added. Evaporates were evaporated to dry under the nitrogen stream. The solution was prepared from TFA Anhydride - Ethyl Acetate (5: 1, v / v) was prepared, 100µl of this solution was added to the remainder and then mixed and heated the sample at 80c for 10 minutes in heating / flipping. The solution was cooled to room temperature and later the solvent evaporated to dry under the nitrogen stream. 1 ml of methanol was added to the residue. The sample was ready for injection in GC MC.

RESULTS AND DISCUSSION

Synthesis of MIPs for Methamphetamine (MAMP)

Two MIPPs of MAMP were installed by self-assembly (non-covalent) bulk polymerization method. Functional monomers have been instrumental in studying interactions with template, Two monomers were used 2-Vinyl pyridine (2-VP), (2-hydroxy ethyl methacrylate)(2-HEM) for the synthesized the MIPs and NIPs.

FTIR Analysis

Figure (2) and (3) show the FTIR spectra (before and after the removal of template) for MIP based on (2-VP) as a Basic functional monomer. The main peaks obtained from figures list in the table (1).

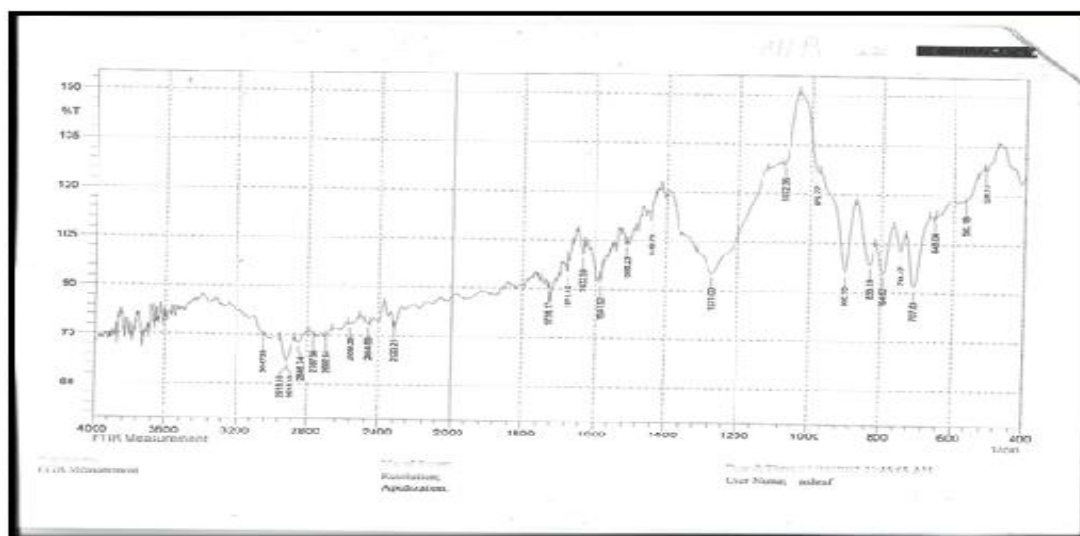


Fig. 2: FTIR of MAMP-MIP (2-VP) before the removal of (MAMP)

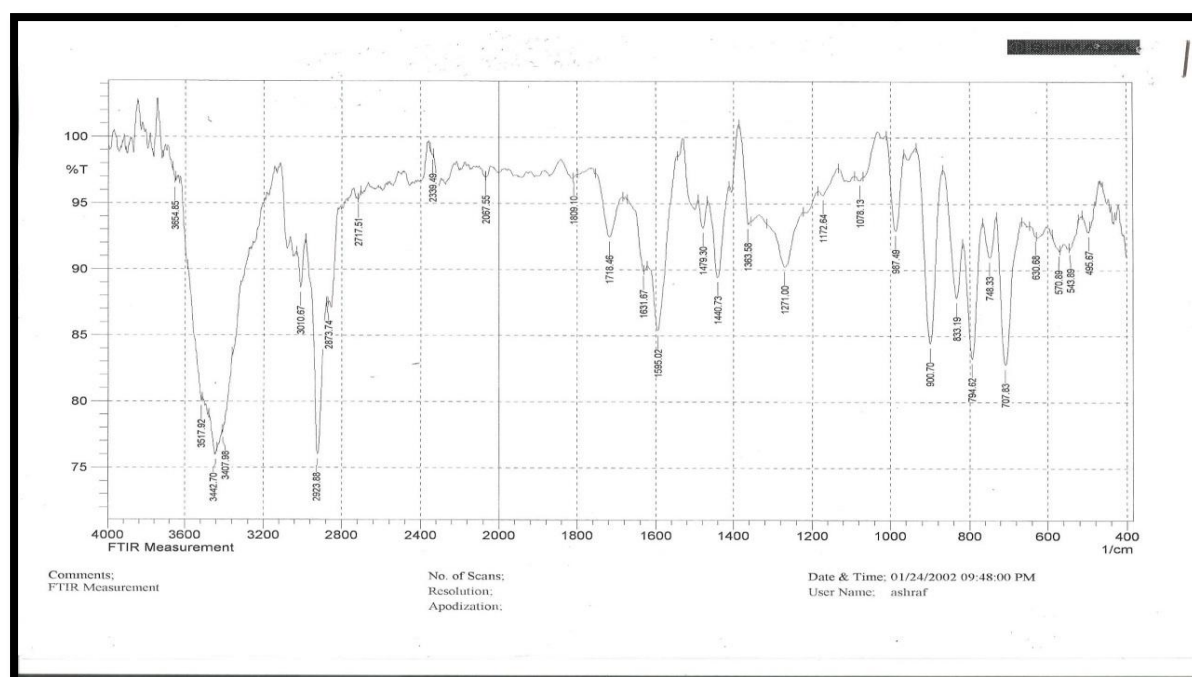


Fig. 3: FTIR of MAMP-MIP (2-VP) after the removal of (MAMP)

Table 1: The most identified peaks of FTIR spectra for MAMP-imprinted polymer and NIP using (2-VP) as a functional monomer

	Functional Group	MAMP	MAMP –MIP(2-VP) before template removal	MAMP–MIP(2-VP) after template removal
1	N-H str. (cm ⁻¹)	3456	3047	----
2	C-H aliphatic.(cm ⁻¹)	2968,2835	2918,2846	2923,2873
3	C=O str.ester.(cm ⁻¹)	----	1726	1718
4	C=C str. (cm ⁻¹)	1596	1581	1595
5	C-H aromatic.(cm ⁻¹)	3159,3016	3047	3010
6	C-H bending (cm ⁻¹)	1483	1471	1456
8	Out-of plane-mono-sub	748,700	794,707	----
9	Out-of plane-para-sub	----	833	833
10	C-O str.ester.(cm ⁻¹)	----	1271	1271
11	C=C str.olefin (cm ⁻¹)	-----	1633	1631

The Fourier transmission infrared spectrometry spectra of leached and un leached methamphetamine (MAMP) imprinted polymers MIP and NIP were recorded in the range of 400–4000 cm⁻¹ by the KBr pellet method (Table 1). From the table 1, the FTIR spectrum of the MAMP shows the following bands: (3456, 3016, 2968, 2835, 1596, 1483, 748 and 700) cm⁻¹ for N-H stretching, C-H aromatic stretching, C-H. Aliphatic stretching, C=C stretching, C-H bending and out of plan bending for mono substituted ring. The FTIR spectrum of the MAMP –MIP (2-VP) before template removal shows the following bands (3047, 2918, 2846, 1726, 1581, 3047, 1475, 794, 707, 833 and 1271) cm⁻¹ for N-H stretching, C-H aliphatic stretching, C=O stretching ester, C=C stretching, C-H aromatic stretching, C-H bending and out of plan bending for mono substituted ring, out of plan bending for para substituted ring, C-O-C stretching and C=C stretching olefin. The FTIR spectrum of the MIP (2-VP) after template removal shows the absence of N-H stretching, C=C stretching and disappear the band of C=O stretching ester, out of plan bending for mono, para substituted ring and C=C str.olefin which excise in template (MAMP) spectrum which indicate the extracted of drug from template.

Figure (4) and (5) show the FTIR spectra (before and after the removal of template) for MIP based on (2-HEMA) as acidic functional monomer. The main peaks obtained from figures list in the table (2).

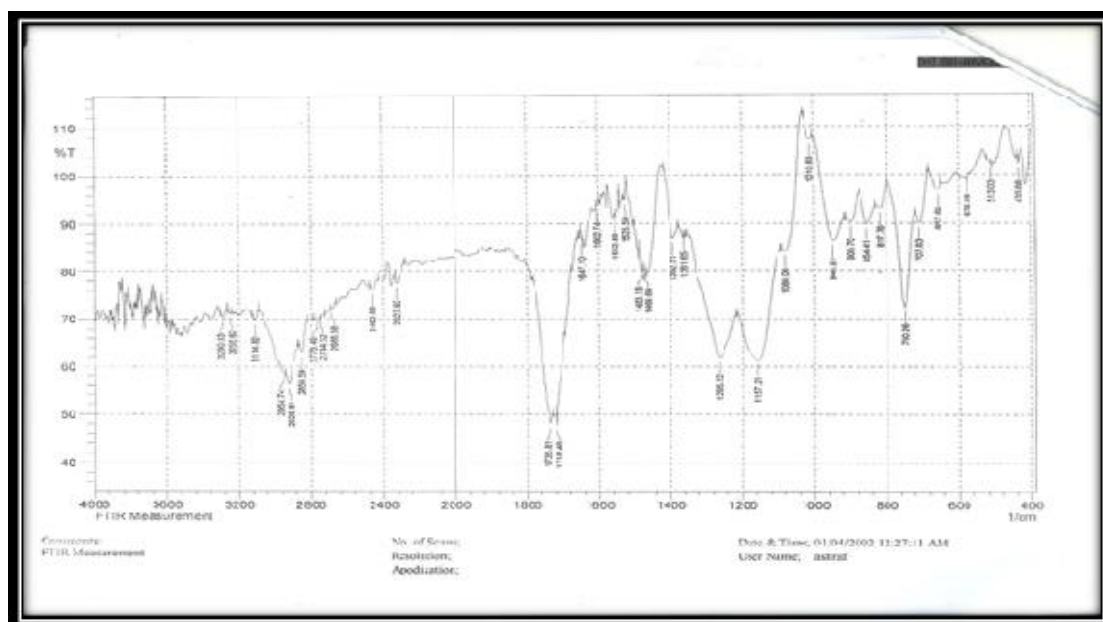


Fig. 4: FTIR of MAMP-MIP (2-HEMA) before the removal of (MAMP)

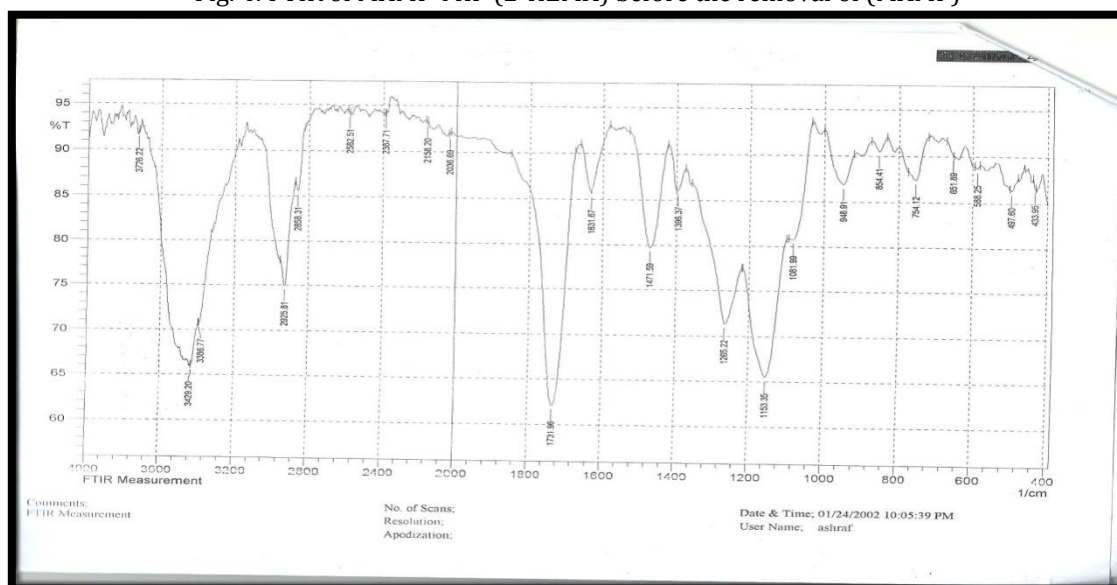


Fig. 5: FTIR of MAMP-MIP (2-HEMA) after the removal of (MAMP)

Table 2: The most identified peaks of FT-IR spectra for MAMP-imprinted polymer and NIP using 2-HEMA as a functional monomer

	Functional Group	MAMP	MAMP -MIP(2-HEMA) before template removal	MAMP-MIP(2- hydroxy ethyl methacrylate)after template removal
1	N-H str. (cm ⁻¹)	3456	3114	----
2	C-H aliphatic.(cm ⁻¹)	2968,2835	2954,2850	2923,2873
3	O-H str.(cm-1)	----	3114	3429
4	C=O str.ester.(cm ⁻¹)	----	1735,1718	1731
5	C=C str. (cm ⁻¹)	1596	1602	----
6	C-H aromatic.(cm ⁻¹)	3159,3016	3047	3010
7	C=C str.olefin (cm ⁻¹)		1647	1631
8	Out-of plane-mono-sub	748,700	750,707	-----
9	C-O str.ester.(cm ⁻¹)	----	1265	1265

From the table (2), the FTIR spectrum of the MAMP shows the following bands: (3456, 3016, 2968, 2835, 1596, 1483, 748 and 700) cm^{-1} for N-H stretching, C-H aromatic stretching, C-H. Aliphatic stretching, C=C stretching, C-H bending and out of plan bending for mono substituted ring. The FTIR spectrum of the MAMP -MIP (2-VP) before template removal shows the following bands (3114, 2954, 2850, 3290, 1735, 1718, 1602, 3047, 1647, 750, 707, 1265 and 1647) cm^{-1} for N-H stretching, C-H aliphatic stretching, O-H stretching, C=O stretching ester, C=C stretching, C-H aromatic stretching, C=C stretching olefin, out of plan bending for mono substituted ring and C-O-C stretching. The FTIR spectrum of the MIP (2-VP) after template removal shows the absence of N-H stretching, C=C stretching, C=O stretching ester and disappear the band of O-H stretching band, C=O stretching ester, C=C str.olefin and C-O str.ester. (cm^{-1}). Several trials were performed using different ratios of (D:M:C) to find out the optimal ratio for the preparation of MIPs (MAMP). Among these trials the molar ratios (D: M: C) of (1:2:10) and (1:3:4) for MAMP-MIPs has produced polymer with very suitable performance characteristics. These ratios are in consistence with some prepared MIPs found in literature. Table (3) summarize the optimum ratios used in the synthesis of MIPs and NIPs for (MAMP) drug.

Table 3: The variation ratios of [D:M:C] and progeny used in the preparation of MIPs and NIPs for (MAMP)

		Drug MAMP	Monomer (2VP)	Cross linker	Initiator	Solvent	Result
MIP3	%	4.3	8.7	87	0.3	5 mL CHCl_3	Pile yellow Gel
	Mmole	0.5	1.00	10.00	0.32		
MIP3	%	2.4	42.4	73.2	0.3	5 mL CHCl_3	Pile yellow Gel
	Mmole	0.5	5.00	15.00	0.32		
MIP3	%	7.6	15.2	76	0.3	mL CHCl_3 7	white rigid
	Mmole	1.00	2.00	10.00	0.32		
NIP3	%	----	15.2	76	0.3	mL CHCl_3 7	white rigid
	Mmole		2.00	10.00	0.32		
		Drug MBV Mmole	Monomer (2-HEMA)	Cross linker	Initiator	Solvent	Result
MIP4	%	11.1	22.2	66.7	0.3	5 mL CHCl_3	Pile yellow rigid
	Mmole	1.00	2.00	6.00	0.32		
MIP4	%	14.3	42.3	42.3	0.3	mL CHCl_3 7	white rigid
	Mmole	1.00	3.00	3.00	0.32		
MIP4	%	12.5	3.75	50	0.3	5 mL CHCl_3	Pile yellow rigid
	Mmole	1.00	3.00	4.00	0.32		
NIP4	%	----	3.75	50	0.3	5 mL CHCl_3	yellow rigid
	Mmole		3.00	4.00	0.32		

All ratio prepared in water bath at 60 C°

On the other hand the control NIPs and MIPs after the removal of template have the similar spectra indicating the similarity in the backbone structure and prove that washing the MIP particles with 70% acetic acid solution used a Soxhlet extraction system is an efficient way to remove the template molecule leaving specific recognition binding sites in the polymer structure.

Adsorption Isotherm

The absorption of isotherm in the understanding of the adsorption mechanism of the adsorption mold with polymer surface. The data obtained from isothermal equilibrium was analyzed to show the isochromatic type of LANGMUIR or Freundlich models [21]. This is determined by plotting the binding capacity (Q) versus the free concentration of the drug, and Q is calculated according to the following equation:

$$Q = [(C_i - C_f) V_s * 1000] / M_{MIP}$$

C_i = initial drug concentration ($\mu\text{mol} / \text{mL}$)

C_f = final drug concentration ($\mu\text{mol} / \text{mL}$)

V_s = volume of solution tested (mL)

M_{MIP} = mass of dried polymer (mg)

Then measuring binding parameter

MIP/drug binding calculated by Scatchard analysis using the equation

$$Q / C_f = (Q_{\max} - Q) / K_d$$

Q_{\max} = maximum capacity

K_d = dissociation constant at binding side.

Isotherm adsorption obtained after shaking different concentrations of MAMP with a synthesis particle for 2 hours in a thermal water bath at 25 ° C as given in in fig (6) . Experimental data for regrouping experiments were included in Table (4).

Table 4: Rebinding values of (MAMP) using MAMP -MIP particles based on (2VP) and (2-HEMA)

MAMP-MIP(2VP)					MAMP-MIP(2-HEMA)			
Mass of	C_i mM	C_{free} mM	Q $\mu\text{Mole} / \text{g}$	Q/ C_{free} L/g	C_i mM	C_{free} mM	Q $\mu\text{Mole} / \text{g}$	Q/ C_{free} L/g
0.2	0.2010	0.1574	2.18	13.85	0.2010	0.1605	2.025	12.6168
	0.4020	0.3102	4.59	14.796	0.4020	0.3128	4.46	14.2583
	0.6030	0.518	2.25	8.204	0.6030	0.5312	3.59	6.7582
	0.8040	0.726	3.9	5.3719	0.8040	0.7419	3.105	4.1852
0.4	0.2010	0.1472	1.345	9.1372	0.2010	0.1307	1.7575	13.4468
	0.4020	0.2993	2.5675	8.5783	0.4020	0.2793	3.0675	10.9828
	0.6030	0.4605	3.5625	7.7361	0.6030	0.4727	3.2575	6.8912
	0.8040	0.671	3.325	4.9552	0.8040	0.6831	3.0225	4.4246

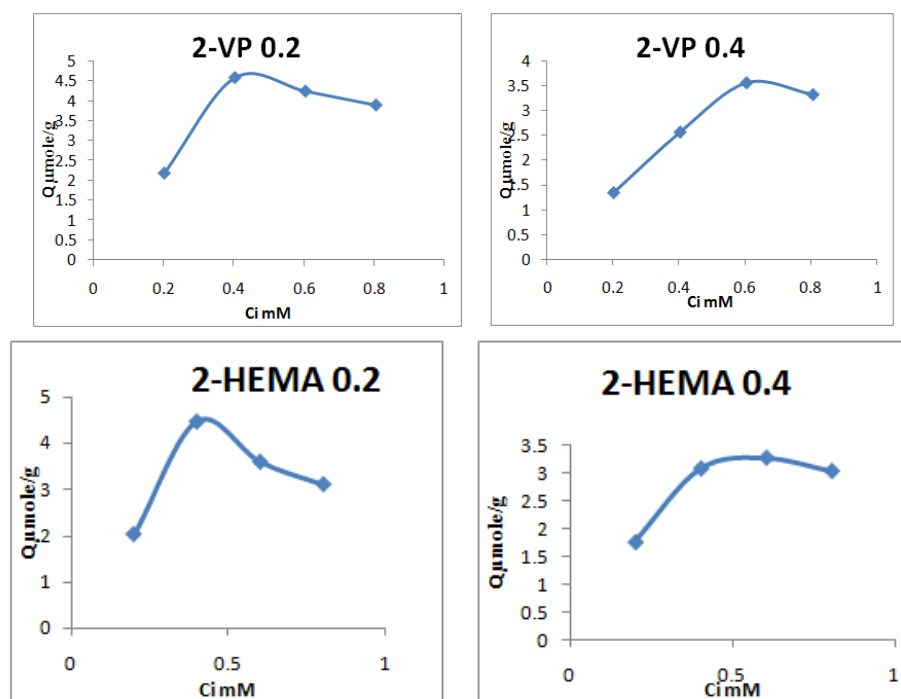


Fig. 6: Binding isotherm of 2-VP and 2-HEMA monomers by plotting Q against C_i

Plots in figure (6) for (2-VP and 2-HEMA) monomers indicates that the binding capacity increase with increasing the concentration of the drug.

The Scatchard plot for 2-VP as monomer shows not linear which means the binding sites were homogenous and gives one type of isotherm adsorption. The plot of Q against Q/C_f gives only one line which is higher affinity binding sites.

The K_d and Q_{max} are 0.8436 mM and 2.627 $\mu\text{mole/g}$ respectively for 0.4 2-VP and for 0.2 2-HEMA K_d and Q_{max} are 3.528 mM and 2.262 $\mu\text{mole/g}$. Scatchard plot of 0.4 2-HEMA is shown in figure (7 and 8).

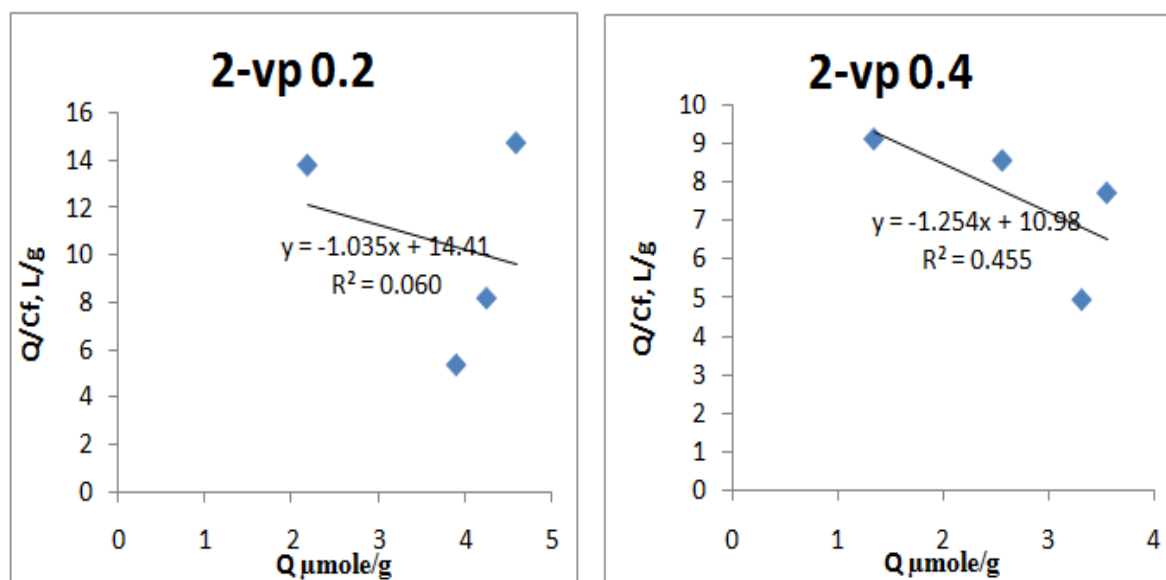


Fig. 7: Scatchard plot of MAMP -MIP based on (2-VP) as a functional monomer

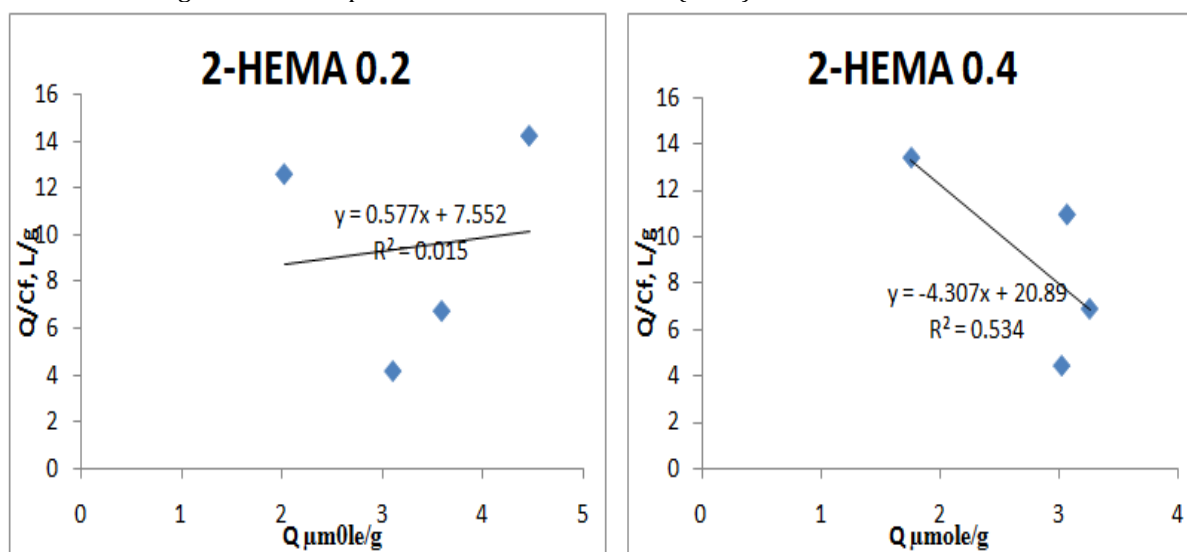


Fig. 8: Scatchard plot of MAMP -MIP based on (2-HEMA) as a functional monomer

Morphological Characterization

Scanning electron microscopy (SEM) was used for primary evaluation of the Imprinted Polymer particles, obtained with different methods.

Fig.(9and10) shows the SEM images of the prepared polymers. It can be seen that the views of the polymer particles are different considerably, depending on the method of the Imprinted Polymer preparation.

Microemulsion polymerization gives very small particles. Spherically shaped polymeric particles with small sizes around (5300-6400)nm for (2-VP) polymer and (3500-4,000) nm for (2-HEMA) imprinted polymer can be distinguished in the related image.

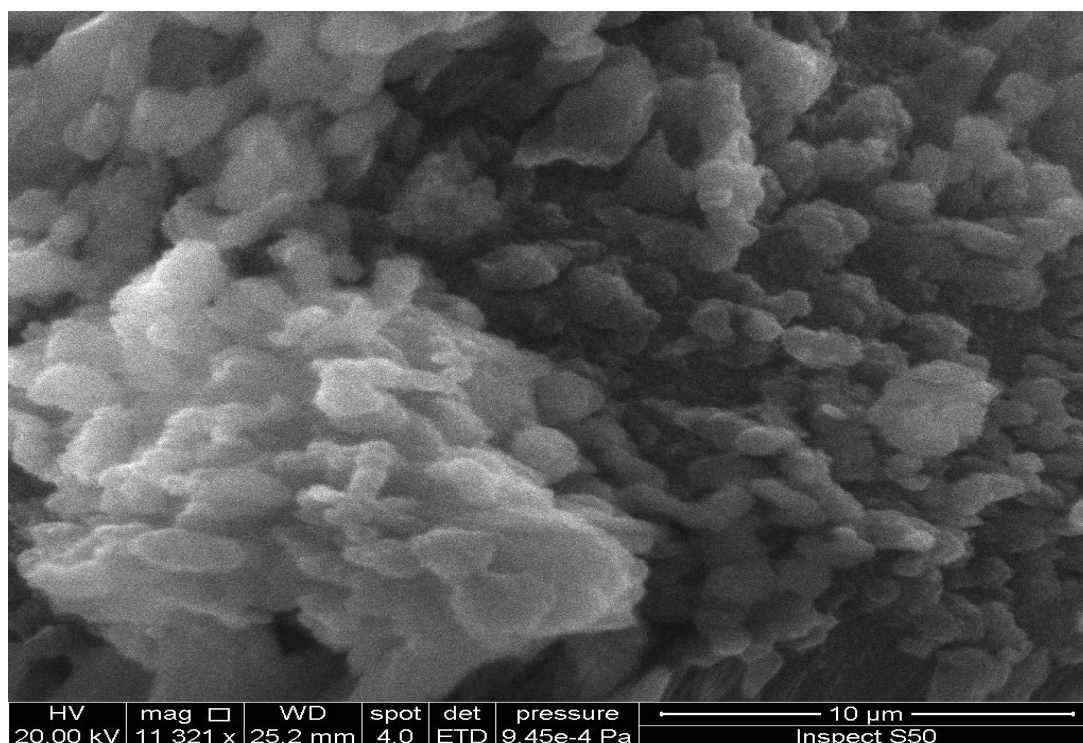


Fig. 9: SEM of [MAMP-MIP(2-VP)] (10µm) obtained by bulk polymerization

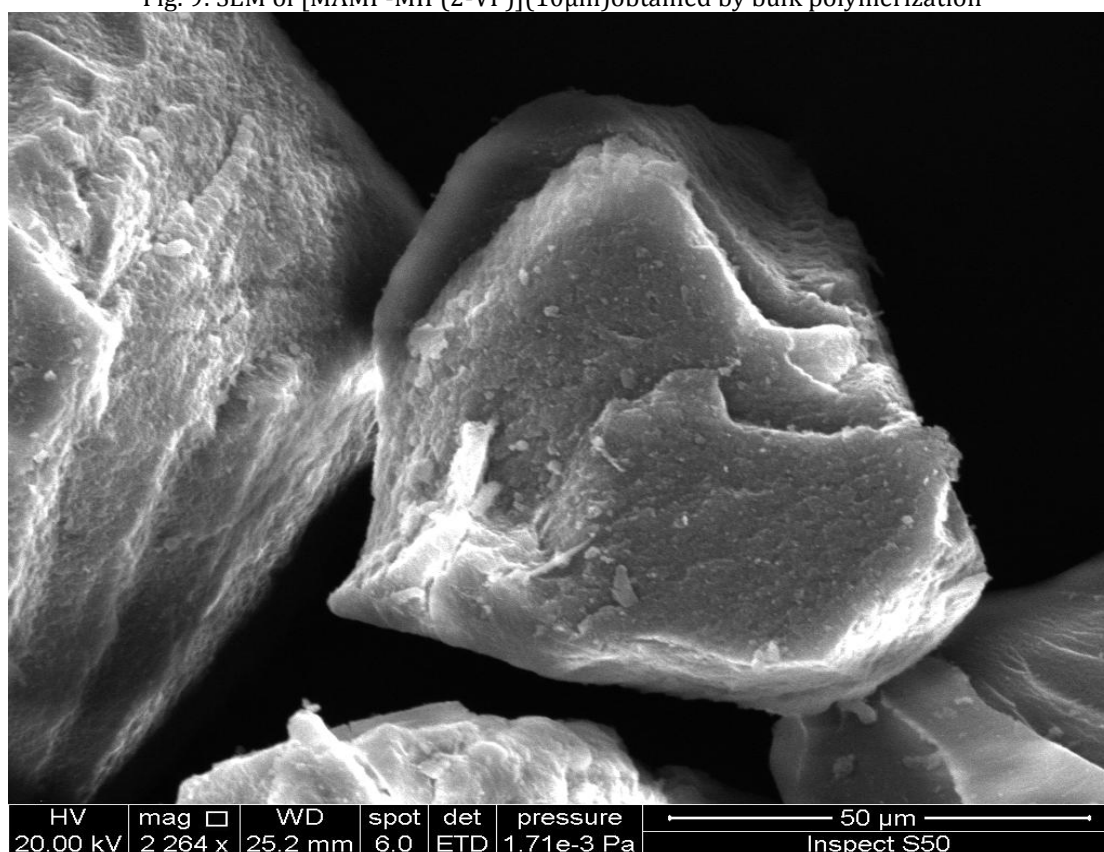


Fig. 10: SEM of [MAMP-MIP(2-HEMA)] (50µm) obtained by bulk polymerization

Effect of Flow Rate

As we noticed that the flow rate of peristaltic pump used for extraction of the **MAMP** from the extraction needle is an important for the time needed for extraction. The flow rate of the sample solution through the fabricated extraction needle is an important factor because it controls the total analysis time and must be enough to prevent waste of time. The flow rate, on the one hand, must be low enough to make an effective retention of the analyte. Therefore, to evaluate the influence of the time of contact

between the MIP and the sample solution on the recovery, the effect of the sample loading flow rate has been studied in the range of 10-100 rpm. show the figures(11 and 12).

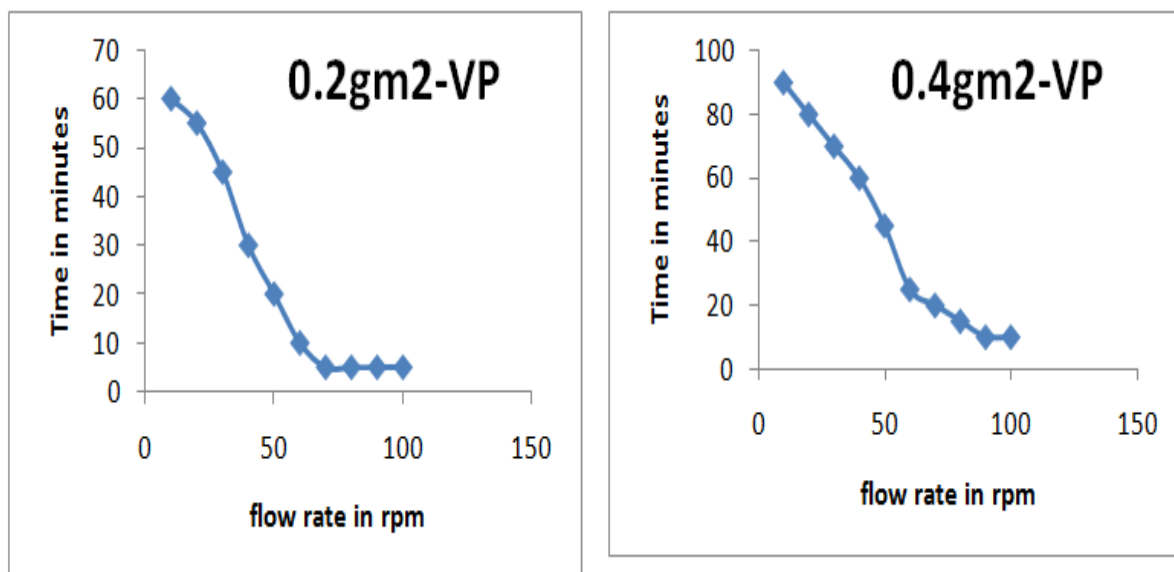


Fig. 11: Relationship between the flow rate and extraction time based on 0.2 and 0.4 gm of MAMP MIP(2-VP) used 60ppm from MAMP

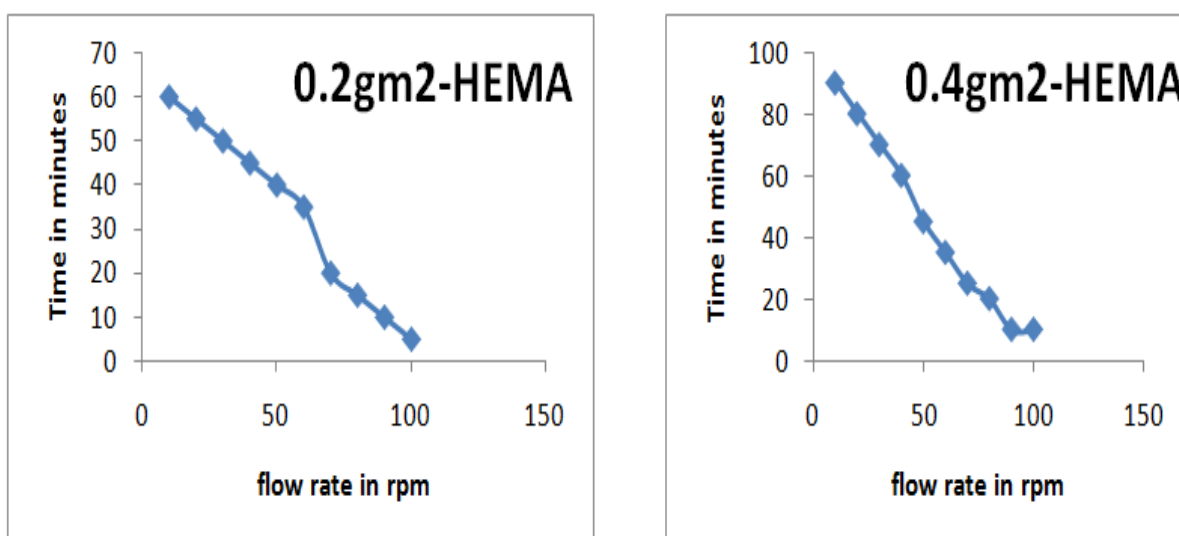


Fig. 12: Relationship between the flow rate and extraction time based on 0.2 and 0.4 gm of MAMP-MIP (2-HEMA) used 60ppm from MAMP

Urine Samples Analysis

Under optimal conditions, MIP-2-VP and MIP-2-HEMA were applied homogeneously to identify methamphetamine in urine samples. The sample matrix of the urine was in the first step and the wash step after the extraction was done. The washing step can be realized by allowing the solution of the carrier, solution of phosphate buffer, to flow through the plastic syringe used for the perstic pump. The components that suck weakly into a homogeneous column are expected to be removed by the washing step. By extending the washing time from 75 seconds to 3 minutes, the matrix tops were clearly suppressed.

This can be demonstrated by extracting an empty urine sample with a wash step of 3 minutes. The application of the same washing step to the urine sample rose, achieved satisfactory results of methamphetamine: no decrease was found in height of the analytes compared to those obtained by extracting standard samples. That were taken plastic syringe contains 0.2-0.4 g of MIP (2-VP) and MIP (2-HEMA) with passing different concentration of methamphetamine in urine samples was achieved in a range of 30-150 ppm successfully under optimal conditions. The results are shown in table 5 and 6.

Table 5: Standard addition method for drug determination using imprinted polymer method solid phase extraction used MIP-2-VP.

Wt. of MIP (g)	Conc. of solution (ppm)	Synthetic solution		% Recovery	No. of Patients	*Drug conc. (ppm)	% Recovery	RSD%
		Conc. Taken (ppm)	Conc. Found (ppm)					
0.2	30	30	29.44	98.13	1	28.23	94.10	2.47
					2	28.09	93.63	3.53
					3	28.85	96.16	2.58
					4	29.23	97.43	1.89
					5	29.51	98.36	2.02
0.2	60	60	59.72	99.53	1	59.24	98.73	1.47
					2	58.35	97.25	1.39
					3	59.14	98.56	2.46
					4	59.01	98.35	2.65
					5	58.65	97.75	1.98
0.4	30	30	29.83	99.43	1	29.14	97.13	2.87
					2	29.76	99.20	1.48
					3	29.40	98.00	1.29
					4	29.55	98.50	2.57
					5	29.68	98.93	2.78
0.4	60	60	59.87	99.78	1	59.83	99.71	2.18
					2	59.76	99.60	1.59
					3	59.51	99.18	1.89
					4	59.30	98.83	1.32
					5	59.03	98.38	1.86

Average of three measurements

Table 6: Standard addition method for drug determination using imprinted polymer method solid phase extraction used MIP-2-HEMA

Wt. of MIP (g)	Conc. of solution (ppm)	Synthetic solution		% Recovery	No. of Patients	*Drug conc. (ppm)	% Relative error	RSD%
		Conc. Taken (ppm)	Conc. Found (ppm)					
0.2	30	30	29.8	99.33	1	28.91	96.36	2.46
					2	29.78	99.26	3.61
					3	29.69	98.96	2.19
					4	29.03	96.76	1.98
					5	28.94	96.46	2.11
0.2	60	60	59.13	98.55	1	58.87	98.11	1.67
					2	59.30	98.83	1.34
					3	59.18	98.63	1.29
					4	59.45	99.08	1.55
					5	59.49	99.15	1.98
0.4	30	30	29.61		1	28.11	93.70	2.89
					2	29.09	96.96	3.12
					3	29.82	99.40	2.67
					4	28.95	96.50	1.98
					5	29.89	99.63	2.84
0.4	60	60	59.28	98.80	1	59.78	99.63	2.65
					2	59.61	99.35	1.87
					3	58.59	97.65	1.20
					4	58.68	97.80	1.73
					5	59.58	99.30	2.16

Average of three measurements

The values in Table 5 and 6 reflect the use of MIP a technique to detect the methamphetamine and estimated it used GC-Mass. The results obtained were for the methamphetamine and its derivatives as found in the applied forms, show figures 13, 14 and 15.

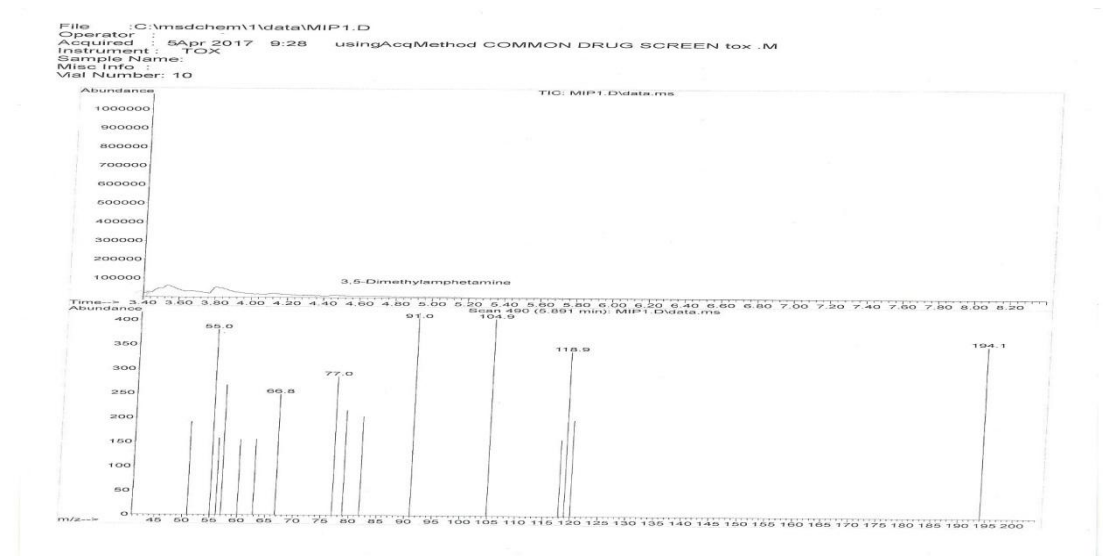


Fig. 13: Structure of methamphetamine derivatives (3,5-Dimthylamphetamine).

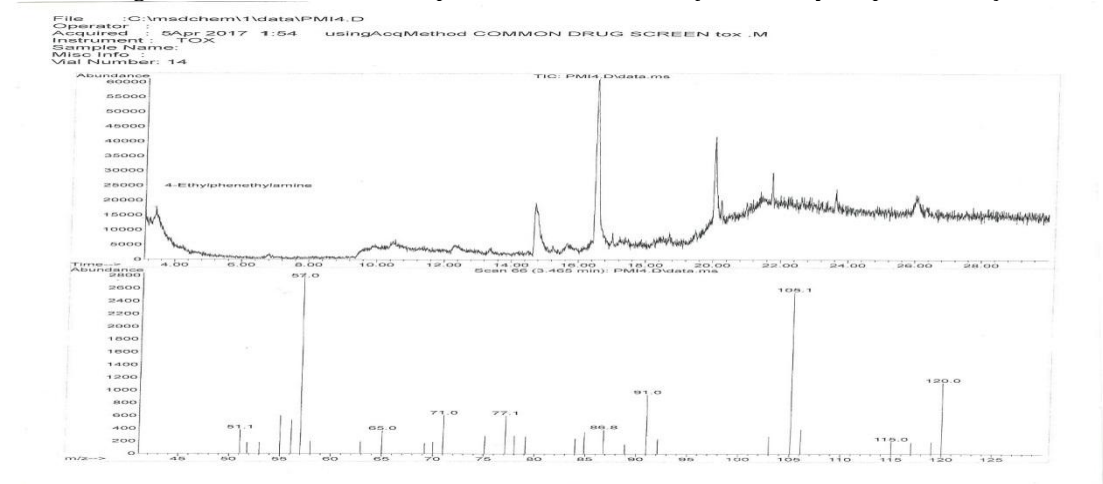


Fig. 14: Structure of methamphetamine derivatives (4- Ethylphenethylamine).

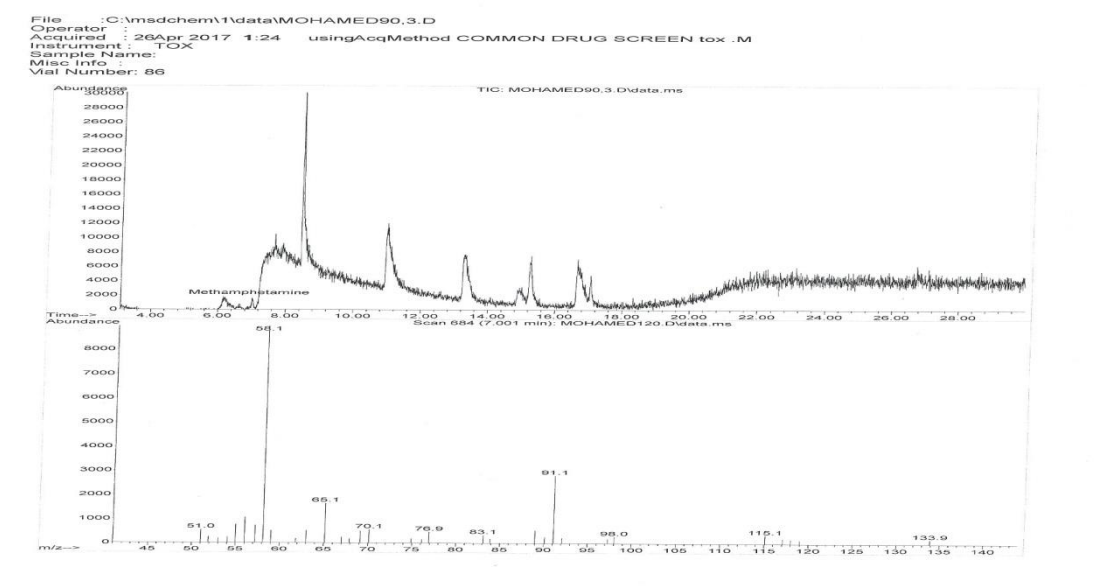


Fig. 15: Structure of methamphetamine

CONCLUSION

In this study, methamphetamine was extracted from the urine samples using MIP methamphetamine solid phase extraction (SPE) Column. The preparation of chemical sensors using different monomers with cross-linker to give the appropriate geometric shape to obtain the molecularly imprinted polymers (MIP), as well as knowledge of the capacity of each imprinted prepared for the methamphetamine and related drugs. Two monomers were used, 2-vinylpyridine (2-VP) and 2-hydroxy ethyl methacrylate (2-HEMA). The drug can be estimated on the basis of small concentrations and multiple mixtures. The first step was to prepare the molecularly imprinted polymers of Methamphetamine, where it is possible to concentrate and estimate small percentages of the drug and at different times for the metabolism of the drug. The second step was to obtain a concentration using solid phase extraction, thus the combination of a molecularly-imprinted polymer with solid-phase microextraction (SPME) obtaining a pre-concentration and estimation process in one step for better precision, sensitivity and selectivity. The effects of the extraction parameters such as flow rate and effect volume of sample on extraction efficiency of the fiber to MAMP were examined by using gas chromatography–mass spectrometry (GC–MS). The time decrease as the flow rate increase and we fixed the flow rate of 70 rpm in which the time was 5 minutes. The volumes less than 10 mL for MAMP should be selected, exhibited good reproducibility and was considered suitable for the determination of trace levels. The data obtained from the equilibrium of isotherm adsorption were analyzed to show the type of isotherm Langmuir or Freundlich models. The binding capacity increase with increasing the concentration of the drug. Very lower detection limits were achieved in range of 0.8–1.2 ng mL⁻¹. Finally, the MIP fibers were successfully applied for selective extraction of MAMP in urine samples with the relative recoveries ranging from (93.70–99.63).

REFERENCES

- [1] Bar AM, Panenka WJ, MacEwan W, Thornton AE, Lang DJ, Honer WG, Lecomte T (2006) *J Psychiatry Neurosci* 31:301–313.
- [2] Pichini S, Pacifici R, Pellegrini M, Marchei E, Lozano J, Nurillo J, Vall O, Garcia-Algar O (2004) *Anal Chem* 76:2124–2132.
- [3] Hendrickson HP, Milesi-Halle A, Laurenzana EM, Owens SM (2004) *J Chromatogr B* 806:81–87.
- [4] Lord HL, Pawliszyn J (1997) *Anal Chem* 69:3899–3906 12. Chia KJ, Huang SD (2005) *Anal Chim Acta* 539:49–54.
- [5] Fan Y, Feng Y, Zhang J, Da S, Zhang M (2005) *J Chromatogr A* 1074:9–16
- [6] Cormack PAG, Elorza AZ (2004) *J Chromatogr B* 804:173–182
- [7] Fan Y, Feng Y, Zhang J, Da S, Zhang M (2005) *J Chromatogr A* 1074:9–16
- [8] Cormack PAG, Elorza AZ (2004) *J Chromatogr B* 804:173–182
- [9] Andrade R, Reyes FGR, Rath S (2005) *Food Chem* 91:173–179
- [10] Zhou F, Li X, Zeng Z (2005) *Anal Chim Acta* 538:63–70
- [11] Djozan Dj, Pournaghi-Azar MH, Bahar S (2004) *Chromatographia* 59:595–599
- [12] Djozan Dj, Assadi Y (2001) *Anal Chem* 73:4054–4058
- [13] Gierak A, Seredych M, Bartnicki A (2006) *Talanta* 69:1079–1087
- [14] Jiang R, Zhu F, Luan T, Tong Y, Liu H, Ouyang G, Pawliszyn J (2009) *J Chromatogr A* 1216:4641–4647
- [15] Mohammadi A, Yamini Y, Alizadeh N (2005) *J Chromatogr A* 1063:1–8
- [16] K.Y.Foo and B.H hameed, insights into the modeling of adsorption iso therm system, review chemical engineering journal 156 (2010) 2-10
- [17] S.Goldberg .Equations and Models Describing Adsorption Processes in Soils Soil Science Society of America, 677 S .Segoe Road, Madison ,WI 53711, USA. Chemical processes in soils. SSSA Book Series, (2005) no. 8.
- [18] Al-Bayati, Y. K.; Aljabari, F. I.; *Asian J. of Chemistry*. 2016, 28(6) 1376-1380.
- [19] Al-Bayati, Y. K.; Al-Saidi, K. H.; Hussain, M. A.; *Asian J. of Chemistry*. 2015, 28(9), 1962-1966.
- [20] Al-Bayati, Y. K.; Al Khafaji, I. H.; *Iraqi Journal of Science*. 2016, 57(4), 2790-2799.
- [21] R. Guadalube, H.E Reynel-Avila, A. Boinilla –Petriciolet, I. Cano-Rodriguez, C. Velasco-Santos, and A.L. Martinez-Hernandez. Recycling Boultry feathers for Pb removal from wastewater: Kinetic and equilibrium studies .Proceedings of World Academy Of Science, Engineering And Technology 2008 Volume 30.