Detection of Methamphetamine using Nanobentonite as a Novel Solid Phase Extraction Column Matrix Assisted with Gas Chromatography- Mass Spectroscopy

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Abstract:

This study was done to evaluate a new technique to determine the presence of methamphetamine in the hair using nano bentonite-based adsorbent as the filler of extraction column. The state of the art of this study was based on the presence of silica in the nano bentonite that was assumed can interact with methamphetamine. The hair used was treated using methanol to extract the presence of methamphetamine, then it was continued by sonicating the hair sample. Qualitative analysis using Marquish reagent was performed to confirm the presence of methamphetamine in the isolate.The hair sample that has been taken in a different period confirmed that this current developing method can be used to analyzed methamphetamine. This method has an average recovery percentage by 104%. This result was also supported by the precision, linearity, LOD and LOQ, i.e. 0.0775; 0.968; 0.00000256 and 0.000000775, respectively.

Keywords: Extraction column, Hair, Methamphetamine,Nanobentonite

Introduction:

Methamphetamine has been recognized as a therapeutic drug, but nowadays it has been used for illegal purposes[1]. Based on several researches and reports, methamphetamine has been categorized as a highly addictive and psychostimulant drug, that has a similar effect as amphetamine[2,3].

Many researches have been developed to find an efficient and effective method to detect methamphetamine from biological samples[1,4-6]. The matrix of the biological sample can be a suspected body, including hair, saliva, blood, urine, and nail. Every biological sample has different properties and different way to handle for the determination of methamphetamine, also it provides valuable information, i.e., exposure time. From all of those biological matrixes, hair is the best matrix for methamphetamine analysis. A hair sample can be used to analyze methamphetamine without giving us a worry that the methamphetamine will be lost, because hair is just like storage that can keep the drug longer than any kind of biological matrix and the information of how long the suspect uses methamphetamine can be known from every inch of their hair. This is an advantage of hair sample than other biological matrices, for example, urine, the methamphetamine only can be found in urine for a short time, normally for hours[7-9].

The disadvantages of hair as abiological matrixis that it needs to a quite complex pre-analysis procedure compared to urine biological matrix. The pre-analysis procedure includes decontamination, extraction, and instrumental analysis. The extraction step is the quite risk part in the pre-analysis of the drug from hair matrix. Because during this step, we need to choose a certain method to avoid the

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presence of interfering substances, i.e., protein, dyes, lipid, cosmetic, etc.[1, 10, 11].

Because of this complexity, selecting the appropriate preparation technique is important to obtain an effective and efficient method with high accuracy or sensitivity during the measurement of the sample. In the conventional technique, solid-phase extraction (SPE) is a quite famous technique that has been developed for a lot of purposes and combined with the use of high technology, i.e., gas chromatography– mass spectrometry (GC-MS), liquid chromatography – mass spectrometry(LC-MS), and liquid chromatography – mass spectrometry– mass spectrometry (LC-MS/MS). Solid-phase extraction technique is becoming popular due to the presence of a lot of natural and synthetic adsorbent for being used in the extraction column of solid-phase extraction[12-15].

Nano bentonite is the one adsorbent that can be developed as the filler of the extraction column for this purpose. North Sumatera, Indonesia, especially in the village of Sarulla, is well known as the sources of some mineral for adsorbent, i.e., bentonite. Based on literature review, nano bentonite has been known as the popular adsorbent due to its adsorption capacity for adsorbing dyes and heavy metals[16, 17]. Due to the advantages of nano bentonite as adsorbent, it also can be utilized as filler for solid-phase extraction column[18, 19]. Until now, no research has been conducted for this purpose to utilize the nano bentoniteas the filler of the extraction column for methamphetamine determination. In this study, methamphetamine was collected through SPE which contained nano bentonite as the adsorbent, and this collected methamphetamine was then examined using GC-MS.

Materials and Methods:
Materials
The reference compound of methamphetamine was obtained from Laboratorium Satuan Kerja Seksi Pelayanan Teknis Balai pengujian dan Identifikasi Barang, Medan. Natural bentonite was obtained from Sarulla village, Tapanuli Utara regency, Sumatera Utara province. The hair samples were obtained from the rehabilitation center Datuk Etham, Tanjung Morawa, Sumatera Utara, Indonesia.

Preparation of nano bentonite
Nano bentonite was prepared according to the previous method[20]. Bentonite used is bentonite nano particles that have been made using the coprecipitation method. Approximately 20 grams of bentonite powder were dissolved in HCl 12 M 100

ml then heated at around 70°Cfor 120 minutes at 350 rpm. The solution was neutralized by adding distilled water. The solution was placed in oven for 5 hours with a temperature of 100°C. After drying, crushed with mortar to produce powder. Bentonite powder is calcined in the furnace at 600°C. Powder bentonite at a ball mill with a speed of 100 rpm for 30 minutes and then sieved.

Preparation of solid-phase extraction column
About 100 mg of nano bentonite was placed in to the extraction column and conditioned using methanol. (Merck) The conditioned extraction column then neutralized using phosphate buffer saline (Merck).

Preparation of hair matric
Approximately 40 mg of hair samples were pulverized and washed with methanol three times. The specific solvent combined of methanol: acetone: ammonia was added into the pulverized hair sample and sonicated for 30 min and the temperature was kept constant. The hair in this step was then sonicated again using chloroform for 5 min and then liquid-liquid extraction was performed using methanol. To confirm the presence of methamphetamine in the filtrate, the qualitative test was performed using Marquis reagent. The obtained filtrate then injected to the extraction column and eluted with dichloromethane: isopropanol (9:1) to remove the contaminant from the sample. The mixed solution of ethyl acetate: ammonium hydroxide (98:2) was used as eluent to extract the methamphetamine from the extraction column matrix. The obtained eluate then analyzed using GC-MS (Agilent 7890).

Method Validation
The suitability of nano bentonite as the matrix in the extraction column was evaluated by measuring the precision, linearity, limit of detection and limit of quantification.

Result and Discussion:
Characteristic of bentonite
The as-prepared bentonite has been characterized using X-ray fluorescence (XRF) and particle size analyzer (PSA) instruments. Based on XRF result the as-prepared bentonite has a high content of SiO_2 (70.39%) then followed by alumina oxide (15.52%) and other elements. A similar result also obtained in the previous work,silica was obtained as the highest composition in several bentonites and followed by the presence of alumina oxide[21].From the PSA analysis, the as-prepared

bentonite has an average nano sized particle, it was 157.17 nm.

GC-MS result

Methamphetamine was analyzed using GC-MS without any derivatization technique. This method was conducted due to obtaining a simple and fast technique in the forensic application. To obtain sufficient sensitivity for the quantitative analysis, the amount of methamphetamine the hair was observed for 210 days after their abstinence. Table 1 list the quantitative result of methamphetamine from a random hair sample.

Table 1. Methamphetamine amount in the random hair sample

| No | Hair sample | Methamphetamine amount (ng/mg) | | | |
| | | Day (s) | | | |
		0 – 14	60	150	210
1	A	4.62	3.10	2.56	1.95
2	B	3.29	3.13	2.62	1.00
3	C	4.17	3.65	2.59	1.16
4	D	4.61	3.13	2.49	1.81
5	E	4.17	3.28	2.54	1.68

The methamphetamine was positively obtained in all randomized hair sample. This indicates that the users have consumed methamphetamine over 12 months, this also can be seen from the hair length of the users. Kintz[22] stated that the hair sample has several advantages for drugs analysis than urine and blood, i.e. the information of drugs still can be found in weeks or months after the user stopped consuming drugs.

The qualitative analysis of GC-MS (Fig.1) was observed from fragmentation peak that indicated the presence of methamphetamine, i.e. m/z134.1; 91.1; 58.1; and 42.1.
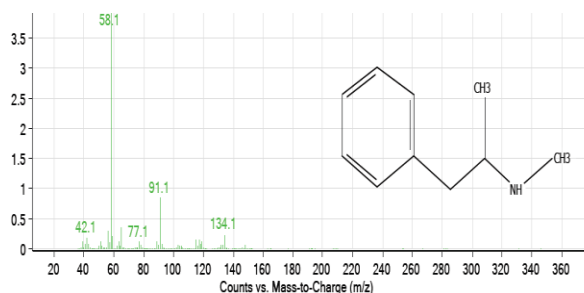
Figure 1. MS spectrum of methamphetamine

Methamphetamine was fragmented into several peaks as can be seen in Figure1 and has a base peak at m/z 58. The fragmentation pattern of methamphetamine can be seen in Fig.2.
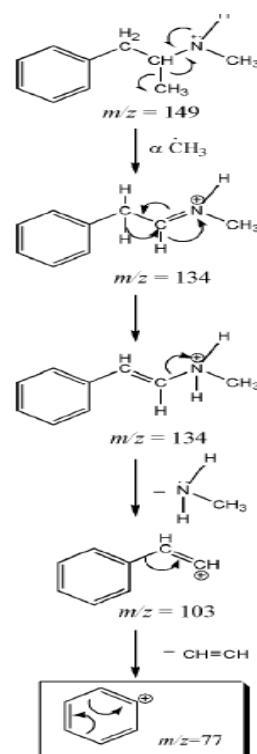
Figure 2. Fragmentation pattern of methamphetamine

Method validation

Method validation was performed to ensure the performing method in an analysis has good repeatability, accuracy and precision. In the current study, the recovery, precision, LOD and LOC has been determined.
The linearity was tested in the concentration ranges of 0-100 ppm. Table 2 presents the calibration parameters such as slope, intercept, LOD and LOQ. The R^2 valuefor the linear regression was 0.968. The calculated limit of detection (LOD) value was 0.00000256 ng/mg, while the lower limit of quantification (LOQ) value was 0.000000775.

Table 2. Method calibration

Compound	Concentration range (ppm)	Linearity (R^2)	LOD (ng/mg)	LOQ (ng/mg)
Methamphetamine	0-100	0.968	0.00000256	0.000000775

The recoveries of methamphetamine wereobtained by quantifying analysis of three samples which has different concentration level with the addition of 2 ng/mg of methamphetamine. From this analysis, the uses of nanobentonite as the matrix of SPE column and GC-MS analysis showed this method has an acceptable value of recovery's percentage, it was about 104%. From the literature, the acceptable recovery's percentage has ranged between 70-120%. The precision of this method

was obtained from the deviation standard that produced from triplicate measurements. The deviation standard and the deviation standard relative of this method were 0.0775 and 1.1725%

Conclusions:

A GC-MS method in a combination with an SPE column used nano bentonite as the matrix is studied and evaluated for detecting methamphetamine in human hair. The experimental result proves that the proposed method is effective to detect methamphetamine in human hair. This method has an average recovery percentage by 104%. This result is also supported by the precision, linearity, LOD and LOQ, i.e. 0.0775;0.968; 0.00000256 and 0.000000775, respectively.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in Universitas Sumatera Utara.

Authors' contributions:

N.A.D.A., Z.A., B.W. and E.D. contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript

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الكشف عن الميثامفيتامين باستخدام النانو بنتونايت كمصفوفة جديدة لعمود استخلاص الطور الصلب بمساعدة كروماتوجرافيا الغاز ـ التحليل الطيفي للكتلة

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الخلاصة:

أجريت هذه الدراسة لتقييم تقنية جديدة لتحديد وجود الميثامفيتامين في الشعر باستخدام الممتزات النانوية البنتونايت كحشو عمود الاستخلاص. استند أحدث ما توصلت إليه هذه الدراسة على وجود السيليكا في النانو بنتونايت الذي يُفترض أنه يمكن أن يتفاعل مع الميثامفيتامين. تمت معالجة الشعر المستخدم باستخدام الميثانول لاستخلاص الميثامفيتامين في عينة الشعر باستخدام جهاز الامواج فوق الصوتية . تم إجراء التحليل النوعي باستخدام كاشف ماركيش لتأكيد وجود الميثامفيتامين في عينة الشعر المستخلصة .أكدت العينات للشعر التي تم أخذها في فترات مختلفة أن طريقة التطوير الحالية يمكن استخدامها لتحليل الميتامفيتامين. هذه الطريقة لديها نسبة استرداد متوسطة بنسبة 104٪. تم دعم هذه النتيجة أيضًا من خلال نتائج الدقة والخطية و LOD و LOQ، وكانت القيم 0.0775 ؛ 0.968 ؛ 0.00000256 و 0.000000775 على التوالي.

الكلمات المفتاحية: عمود الاستخلاص ، الشعر ، الميثامفيتامين ، النانو بنتونايت.

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