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Recent trends in analytical methods and separation techniques for drugs of abuse in hair

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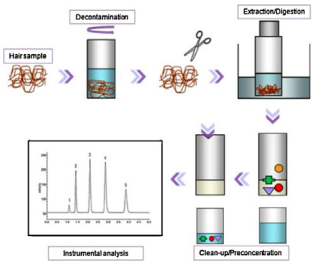
HIGHLIGHTS

- Last trends in analytical methods for drugs of abuse determination in hair are reviewed.
- Recent approaches in hair sample preparation are highlighted.
- Different factors that influence the results interpretation are deeply discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Hair analysis of drugs of abuse has been a subject of growing interest from a clinical, social and forensic perspective for years because of the broad time detection window after intake in comparison to urine and blood analysis. Over the last few years, hair analysis has gained increasing attention and recognition for the retrospective investigation of drug abuse in a wide variety of contexts, shown by the large number of applications developed. This review aims to provide an overview of the state of the art and the latest trends used in the literature from 2005 to the present in the analysis of drugs of abuse in hair, with a special focus on separation analytical techniques and their hyphenation with mass spectrometry detection. The most recently introduced sample preparation techniques are also addressed in this paper. The main strengths and weaknesses of all of these approaches are critically discussed by means of relevant applications.

Tatiana Baciu obtained a Bachelor's degree in Chemistry at the Rovira i Virgili University from Tarragona in 2011 and a Master's Degree in Applied Chromatographic Techniques in a interuniversitary Master organized by the Department of Analytical and Organic Chemistry of the Rovira i Virgili University (URV), the Department of Chemistry of the University of Girona and the Institute of Pesticides and Waters from the Jaume I University in Castelló, in 2012. Currently she is a Ph.D. student in the research group of "Chromatography, environmental applications" of the URV. Her research focuses on novel strategies based on the in-line combination of capillary electrophoresis with different preconcentration techniques in the analysis of biological samples.

Francesc Borrull obtained his Ph.D. in chemistry in 1985 at the University of Barcelona. At present he is a full professor in analytical chemistry in the Department of Analytical and Organic Chemistry of the Faculty of Chemistry at the Rovira i Virgili University (Tarragona). His research is focused on developing new analytical methods for determining emerging organic compounds in environmental samples, using chromatographic techniques and mass-spectrometry detection, with emphasis on the pretreatment systems, specially on the synthesis of new sorbents to be applied in solid-phase extraction techniques. Other activities are focused on the study of preconcentration techniques applied to capillary electrophoresis systems and on the determination of radionuclides in environmental samples. He is the author of about 300 articles in international peer reviewed journals.

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1. Introduction

Drugs of abuse are a major concern that is increasingly affecting every sector of society. Consequently, there is a need for the continuous development of methods for the efficient determination of drugs of abuse and their metabolites in biological samples. The benefits of hair analysis are numerous [1–12]. The ability to detect past drug consumption is a unique feature of this matrix, as it provides researchers with a longer detection window (months to years). Assuming hair grows approximately 1 cm per month, segmental analysis of hair strands allows the determination of the historic pattern of drug use [4,13–18]. Additional advantages of testing hair include a non-invasive means of easily supervised sample collection, reduced risk of sample adulteration, easy sample storage and transportation, and reduced risk of exposure to biohazards. As such, hair analysis of illicit drugs and pharmaceuticals is currently employed to address a wide range of challenges including drug abuse history, workplace testing, post-mortem toxicology, therapeutic drug monitoring and drug facilitated assault (DFA) investigations [1,3,4,7,10,11,19–21].

The mechanism of incorporation of xenobiotics into hair has not yet been clearly defined, but there are several potential mechanisms, as shown schematically in Fig. 1, which are generally accepted among the scientific community: passive diffusion from blood capillaries during hair formation, deposition by diffusion from sebum or sweat secretions into the hair follicle after formation, and from the external environment [3,5–26]. According to the passive diffusion model, excretion of drugs in hair should be delayed a few days because new hair takes some time to emerge from the skin surface and be available for sampling [6,14,21,27–29]. The chemical properties of the incorporated drugs, as well as the physical/physiological characteristics of the individual, strongly influence which mechanism will dominate. Three key factors influence drug incorporation. These are the melanin content of hair and the lipophilicity and basicity of the substance itself: pigmented hair will contain higher drug amounts and, lipophilic and basic drugs will be more concentrated [3,5,9,11,22,30,31]. Externally, drugs can be deposited on hair from the environment via smoke, pollution or physical contact, chemicals, etc. (Fig. 1), leading to false-positive results [9,26,29,32,33]. With this in mind, the Society of Hair Testing (SoHT) and Substance Abuse and Mental Health Services Administration (SAMHSA) produced a set of recommendations (wash-out analysis, metabolite identification, cut-off values) that were shown to be helpful for an appropriate interpretation of the results [19,20]. Later in this paper, there is a discussion of the fundamental factors to take into consideration when interpreting analytical results (external contamination, cosmetic treatments, hair colour, differences in hair growth rate).

In the case of abusers, most drugs are expected to be found in hair in the ng mg^{-1} range; cannabinoids are usually found at lower concentrations (pg mg^{-1}) and 11-nor-Δ^9-tetrahydrocannabinol-9-carboxylic acid (THC-COOH) is even less concentrated. In recent years, it has been shown that a single exposure to a drug is detectable in hair in the case of most drugs, with concentrations in the low pg mg^{-1} range being expected, particularly, in DFA cases because drugs are frequently administrated surreptitiously in beverages [2,34,35].

Drug-associated crimes (sexual assault, robbery) are now frequently reported. Drugs used to facilitate sexual assaults are pharmaceuticals such as benzodiazepines (BZDs), hypnotics,

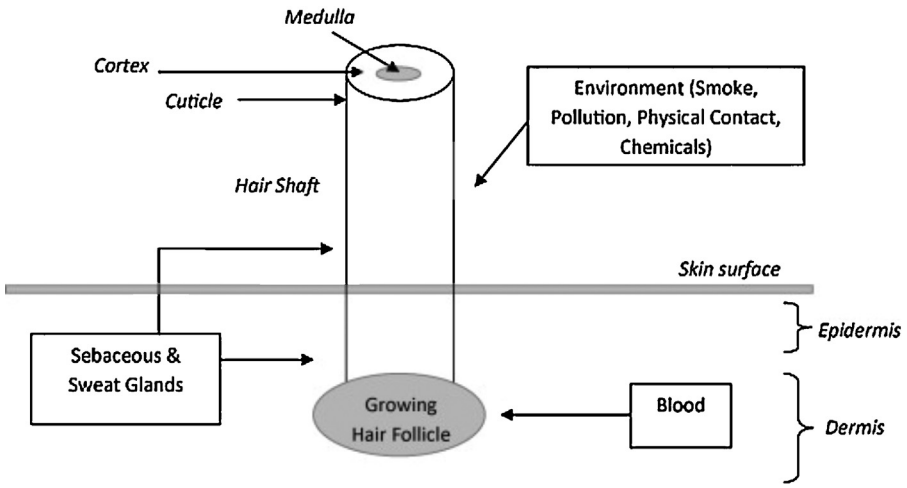

Fig. 1. Schematic of drug incorporation into/onto the hair shaft (reproduced from [215] with the permission of Elsevier, copyright 2010).