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Detection of fingermarks by colloidal gold (MMD/SMD) – beyond the pH 3 limit

Andy Becue *, Aurèle Scoundrianos, Sébastien Moret

Institut de Police Scientifique, School of Criminal Sciences, Building Batochime/University of Lausanne, CH-1015 Lausanne, Switzerland

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ABSTRACT

This work is part of a continuing goal to improve the multimetal deposition technique (MMD), as well as the single-metal deposition (SMD), to make them more robust, more user-friendly, and less labour-intensive. Indeed, two major limitations of the MMD/SMD were identified: (1) the synthesis of colloidal gold, which is quite labour-intensive, and (2) the sharp decrease in efficiency observed when the pH of the working solution is increased above pH 3. About the synthesis protocol, it has been simplified so that there is no more need to monitor the temperature during the synthesis. The efficiency has also been improved by adding aspartic acid, conjointly with sodium citrate, during the synthesis of colloidal gold. This extends the range of pH for which it is possible to detect fingermarks in the frame of the MMD/SMD. The operational range is now extended from 2 to 6.7, compared to 2–3 for the previous formulations. The increased robustness of the working solution may improve the ability of the technique to process substrates that tend to increase the pH of the solution after their immersion.

1. Introduction

Multimetal deposition (MMD) is a well-known fingermark detection technique based on the use of metal nanoparticles in solution. First proposed in 1989 [1], MMD (currently known as "MMD-I") aims at detecting latent fingermarks on a wide range of substrates through a two-step procedure (Fig. 1). First, the deposition of gold nanoparticles onto the latent secretion is promoted under specific experimental conditions. This is followed by a silver-based enhancement step allowing the visualization of the latent fingermarks. As a result, the detected fingermarks appear as dark-brown marks on a most likely unstained substrate and as light marks on dark substrates. An early publication referred to MMD as "The Universal Process" [2]. This denomination was not further retained, but actually emphasized a major strength of the MMD process: its ability to detect marks on a wide range of substrates, being porous, non-porous, or semi-porous. The latter is considered as difficult to process using conventional techniques which are generally limited to strictly porous or non-porous substrates. A good illustration of this versatility is the example given in Saunders' article: the processing of a computer floppy disk. Such an item is composed of three distinct surfaces (i.e., metal, paper, and plastic) and would have required at least two conventional techniques to be applied sequentially to detect fingermarks (one for the paper surface and another for the non-porous ones). The use of MMD-I allows the processing of these three different surfaces simultaneously. Despite this advantage, the success of MMD-I was limited and the technique was seldom applied in casework. Several drawbacks can explain this lack of success: (1) MMD-I is a labour-intensive technique, with several rinsing and immersion baths; (2) it is quite a time-consuming technique, requiring at least 1 h to complete the process; (3) the deposition of the gold nanoparticles onto secretions occurs only if the pH of the colloidal gold solution is set to a precise and narrow range of values (ca. 3.0; outside this range, the efficiency of the method significantly drops, explaining the difficulties encountered with some alkaline papers); (4) the original silver enhancement step takes place quickly, within 1 or 2 min, and could cause unwanted background darkening if the substrate is left too long in the enhancement bath; and, finally, (5) dark-brown marks are obtained, which can be problematic on dark or patterned substrates.

Since 1989, several research projects aimed at increasing the efficiency of MMD as well as its robustness towards experimental conditions (particularly, the pH), in addition to simplifying its experimental protocol (Fig. 2). A major evolution was the development of the "MMD-II", ca. ten years after the MMD-I [3]. Modifications were brought on the colloidal gold synthesis and on the silver-enhancement step, but the overall detection mechanism remained unchanged (i.e., gold deposition followed by metal-based enhancement). Regarding the colloidal gold synthesis, gold nanoparticles of 14 nm (diameter) were preferred to the 30 nm nanoparticles used in the MMD-I, both being monodisperse. The silver enhancement process was also completely modified so that the risk of background darkening was consistently reduced (but not avoided completely). As a result, MMD-II proved to be more robust and more efficient compared to MMD-I, and was consequently proposed as a replacement for the original technique

* Corresponding author. Tel.: +41 021 692 46 30; fax: +41 021 692 46 05.
E-mail address: andy.becue@unil.ch (A. Becue).

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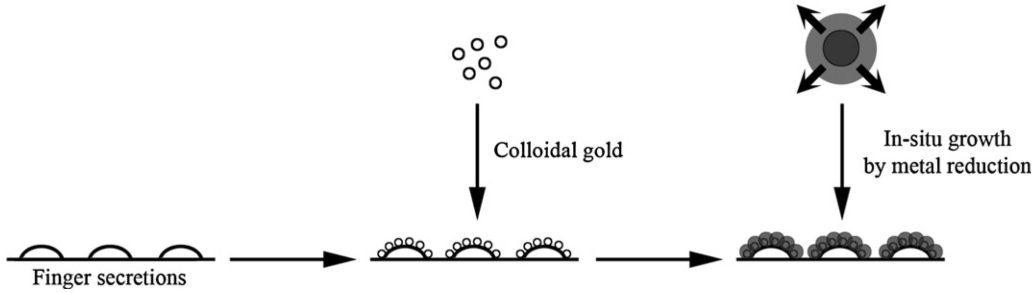

Fig. 1. Schematic illustration of the two steps characterizing the multimetal deposition technique (MMD): gold nanoparticle deposition followed by metal enhancement. This chart is valid for MMD-I, MMD-II, and SMD, which differ in regards with the colloidal gold synthesis protocols or the metal used for the enhancement.
Image source: [16].

[4]. Nevertheless, MMD-II still suffered from major drawbacks: (1) the colloidal gold synthesis is more complex and time-consuming compared to MMD-I; (2) the protocol is still labour-intensive (even if the processing time has been reduced to ca. 40 min compared to MMD-I); and (3) the working solution still needs to be set within a narrow range of pH values, the authors recommending between 2.5 and 2.8. Deviating from these values would result in a drastic drop in the efficiency on MMD-II (especially when the pH is higher than required), with almost no result obtained when working at a pH of 4 or above.

A second major evolution of the technique was the development of the single-metal deposition (SMD) method, proposed as an alternative to MMD-II [5]. The modifications are related to the metal-enhancement step only, the colloidal gold deposition remaining unchanged compared to MMD-II. By replacing the "silver on gold" enhancement mechanism by a "gold on gold" one,

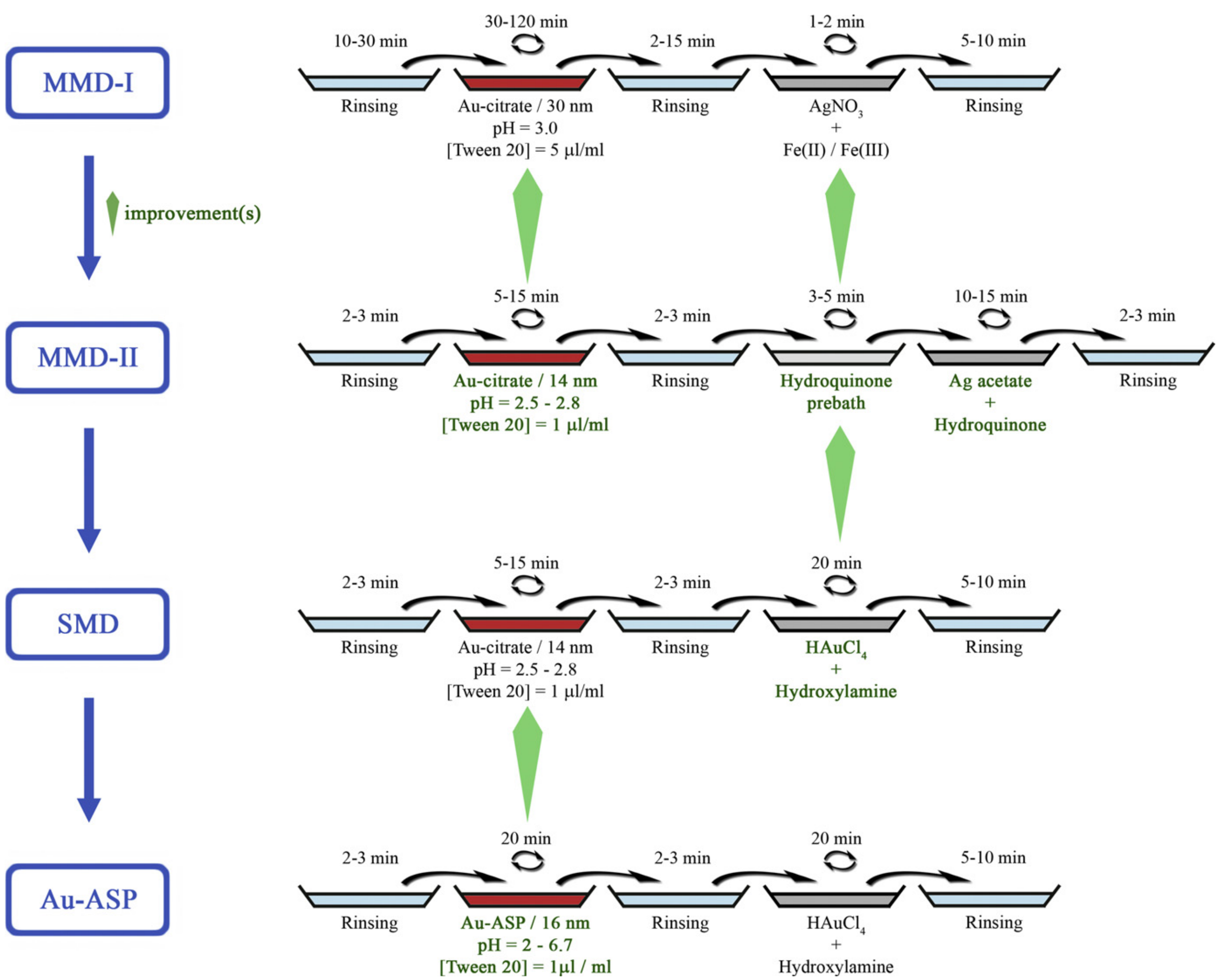

Fig. 2. Evolution of the multimetal deposition technique, from MMD-I to "Au–ASP" (as a premise of a forthcoming "SMD-II"). Each major modification between a technique and its evolution is illustrated by a green arrow.