Forensic Chemistry 3 (2017) 14–20

Contents lists available at ScienceDirect

Forensic Chemistry

journal homepage: www.elsevier.com/locate/forc

Reviews

Comments on the multiple headspace-solid phase microextraction (MHS-SPME) technique for dating inks

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ARTICLE INFO

Article history:
Received 10 September 2016
Accepted 25 October 2016
Available online 2 November 2016

Keywords:
Questioned documents
Ballpoint ink dating
Volatile ink components
Multiple headspace solid phase microextraction (MHS-SPME)
GC/MS

ABSTRACT

A recent article by San Román et al. (2015) treats the problem of determining the age of ink writing using the MHS-SPME technique. Ballpoint pen inks are studied since they tend to age more slowly than other writing inks (i.e., they contain solvents that evaporate more slowly than those in other writing inks). The MHS-SPME technique basically determines, via multiple extraction steps, the fraction β of ink solvent molecules that remain after an extraction from a closed vial. During the extraction process, the molecules in the closed vial must be in a state of equilibrium. Using this fraction and the number of solvent molecules extracted during the first extraction, the total number of solvent molecules in the ink sample can be computed. The authors determine the age of ink via the behavior of β with ink age rather than the behavior of total amount of solvent molecules in the ink with ink age. They found that $\ln\beta$ increases linearly with $\ln t$ where t represents the ink age. The authors also found that β is dependent on the amount of ink examined. The purpose of this presentation is to briefly review the MHS-SPME technique and to address these latter two findings.

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http://dx.doi.org/10.1016/j.forc.2016.10.008
2468-1709/

1. Introduction

The recent article by San Román et al. [1] introduces a novel technique that examines the volatile components of ballpoint pen inks for the purpose of determining their age. The authors use the multiple headspace-solid phase microextraction (MHS-SPME) technique which basically sequentially extracts multiple times the volatile components released from a sample housed in a closed vial. It uses the chemically-coated fiber in the SPME device to collect the volatile components and this fiber is subsequently placed in a gas chromatograph with a mass spectrometer detector (GC/MS) for separating, identifying, and quantifying the volatile components (analytes) removed.

The volatile components are distributed among several regions (phases) within the closed vial, the major ones being the headspace, the sample, and the coated fiber (later the paper on which the ink lays and the inside surface of the closed vial are added). There are four key requirements or conditions that must be met for this technique to work correctly. One is that, during each extraction step, these volatile components should be in a state of equilibrium among the several phases. A second condition is that the partition (distribution) coefficients between the volatile components and each of the phases mentioned remain constant after each extraction step. A third condition (similar to the second one given) is that the volumes of the places where the volatile components reside after reaching equilibrium should also remain constant after each extraction step. The forth condition is that the number of analyte molecules in the SPME coated fiber should be proportional to the peak area of that analyte when it is analyzed in the gas chromatograph.

We will see that the reason for imposing the first three conditions is so that the ratio of the analyte molecules in the SPME coated fiber to the total number of analyte molecules present in the closed vial remains constant for each extraction step.

If these four requirements are met, then a plot of $\ln A_i$, where A_i is the measured amount of a given (or chosen) volatile component (analyte) during the ith extraction, against the extraction number $(i-1)$ is a linearly decreasing graph whose slope is $\ln \beta$. The parameter β is the fraction of the total of number of analyte molecules existing in the closed vial that remain during an extraction step. Knowing β and the amount of analyte extracted during the first extraction, A_1, then the total amount of the analyte, A_T, present in the sample can be computed using an equation given below.

The theory of the multiple headspace-solid phase microextraction technique has been treated by numerous authors. Of note is the article by Ezcuerro et al. [2] and the one by Tena and Carillo [3], both of which are exemplary and have relevant references on the topic.

2. Brief derivation of some relevant equations of the MHS-SPME technique

In the MHS-SPME technique a sample is introduced into a vial, capped with a cap having a septum, heated, and a SPME needle is inserted. Once the volatile components that are emitted into the headspace reach equilibrium among the different phases (or locations) they are in or go into, the SPME needle is removed and inserted into a GC/MS instrument to determine the composition of the components (analytes) in the headspace. A series of peaks result in the chromatogram and the peak area of each is determined. This process is repeated several more times keeping in mind that one has to wait until equilibrium is established.

In what follows the possibility that, after equilibrium is reached, some of the analyte molecules exist in/on the paper and some exist adhered to the inner glass wall of the closed vial is considered.

2.1. Basic definitions

The following definitions will be used in deriving the key equations:

N = The total number of analyte molecules in the closed vial at equilibrium (i.e., the molecules are distributed in the headspace, the coated fiber, the ink sample, the paper, and the inner glass surface of the vial. This is the number of analyte molecules originally in the ink before equilibrium in the closed vial is established.)

Note that the number of analyte molecules can be converted to the mass of the analyte by dividing it by Avogardo's number and multiplying it by the molecular mass of the analyte.

N_f = The number of analyte molecules adsorbed on/in the SPME coated fiber at equilibrium.

Similarly defined are the numbers N_h, N_s, N_p, and N_g which correspond to the number of analyte molecules in the headspace, in the ink sample, in/on the paper, and on the glass, respectively. It then follows that,

$$N = N_h + N_f + N_s + N_p + N_g \tag{1}$$

V_f = The volume of the SPME coated fiber that adsorb the analyte molecules at equilibrium (units are in a chosen unit of volume).

Similarly defined are the volumes V_h, V_s, V_p, and V_g which correspond to the volume of the headspace, the ink sample, the paper, and the glass surface, respectively. The volume of the glass surface can be taken to be the volume of the layers of analyte molecules that adhere to the glass. In essence it is not critical to know how the volumes are defined so long as it is known that such a volume exist. The important thing to know is that these volumes should not change in going from one extraction step to the next (see the third condition given above).

$C_f = \left(\frac{N_f}{V_f}\right)$ = The concentration of the analyte molecules adsorbed on/in the SPME coated fiber at equilibrium (units are in number of analyte molecules per a chosen unit of volume).

Similarly defined are the concentrations C_h, C_s, C_p, and C_g which correspond to the concentration of the analyte molecules in the headspace, the ink sample, the paper, and the glass surface, respectively.

$K_{fs} = \frac{C_f}{C_s} = \frac{\left(\frac{N_f}{V_f}\right)}{\left(\frac{N_s}{V_s}\right)} = \left(\frac{N_f}{N_s}\right)\left(\frac{V_s}{V_f}\right)$ = The distribution (partition) coefficient between the analyte molecules in/on the SPME coated fiber (as concentration in the numerator) and those in the ink sample (as concentration in the denominator).

Since there are five phases in which the analyte molecules can exist (headspace, fiber, ink sample, paper, and glass), there exist a total of $(5 \times 4)/2 = 10$ possible distribution coefficients (also called distribution constants). It is a simple exercise to show that from the following four one can generate the remaining six: K_{hf}, K_{hs}, K_{hp}, and K_{hg}. To show this, the following properties (which are also simple to show) are used: for $j, k, l = h, f, s, p,$ and g

$$K_{jk} = \frac{1}{K_{kj}} \tag{2}$$

$$K_{jk}K_{kl} = K_{jl} \tag{3}$$

Combining Eqs. (2) and (3) yields another useful relation,

$$K_{jk}K_{kl} = K_{jl} = \frac{K_{jk}}{K_{lk}} = \frac{K_{kl}}{K_{kj}} \tag{4}$$