Letter to the Editor

December 14, 2019

Ink Dating – Essentials and Scope of Applicability of the Solvent Loss Ratio Method (SLRM)

Dear Editor:

Re: Lyter, A. (2019). "Analysis of phenoxyethanol: instrumental parameters and effects." *Journal of the American Society of Questioned Document Examiners*, Vol. 22, No. 1, pp. 15-17.

The referenced paper (hereafter referred to as "Technical Note"), discusses two aspects of the application of gas chromatography-mass spectrometry (GC-MS), and more specifically the Solvent Loss Ratio Method (SLRM), for dating ink on documents to which my statements here will be directed:

- **Cleanness and inertness of the GC-MS system.** A clean GC-MS is a must to accurately measure the quantity of ink's high-boiling solvents, such as 2-phenoxyethanol (PE).
- **Scope of Applicability**. The scope of applicability for the SLRM is about six months.

1. Cleanness and inertness of the GC-MS system is a must to accurately measure the quantity of ink's high-boiling solvents, such as phenoxyethanol (PE)

In a 2010 conference paper, when discussing the essentials of the Solvent Loss Ratio Method (SLRM), Gaudreau and Aginsky stated that "[w]hen one analyzes active polar compounds, such as PE, cleanness and inertness of the GC-MS system is pivotal for accurate results" [1].

Contrary to that statement, Lyter, based on the data listed in the above Technical Note, makes a conclusion that "*cleanliness of the instrument has [no] impact upon the … ability [of GC-MS] to accurately and precisely measure the quantity of [ink's] semi-volatile components [such as PE].*"

As discussed below, such a conclusion can be scientifically supported neither by the data contained in the Technical Note nor by any other publications on the subject.

First, as follows from the data listed in Table 1 and the text of the Technical Note, the "*quantitation of PE in standard solution[s]*" was conducted without using an internal standard. The internal standard (IS) is used to ensure accurate quantitative analysis via GC-MS. The use of an IS allows the analyst to compensate for natural variations (e.g. injection volume) occuring when samples are injected via syringe in the injection port of a GC [1]. As the numerical ("quantitative") data listed in Table 1 was obtained without using an internal standard, it is very surprising that the data ideally reproduces the differences between the PE concentrations in all the four standard solutions and shows an ideal directly proportional relationship "normalized PE peak area (Y) – PE concentration (X)."

Second, as follows from numerous scientific publications relating to GC and GC-MS, the relationship "peak area (Y) – analyte concentration (X)"[1] is usually described by a linear function:

$$Y = bX + a \qquad \text{(Eq. 1)}^2$$

where the coefficient a is not equal (or close) to zero.

However, as mentioned above, Table 1 in the Technical Note shows that the relationship between the concentrations of the solvent PE in all four standard solutions (X) and the "normalized" peak areas of the PE in these standard solutions (Y) is a directly proportional one (the coefficient a is equal to zero):

$$Y = bX \qquad \text{(Eq. 2)}$$

The directly proportional relationship "peak area (Y) – analyte concentration (X)" is very atypical for GC and GC-MS. Even the very same publication by Gaudreau and Brazeau [2], which discusses the "SLR method" that Lyter referred to in the Technical Note, clearly shows that, for

[1] Even for the ranges of 'working' concentrations that are substantially narrower than the wide range of PE concentrations in the four standard solutions analyzed by Lyter – from 0.1 ng/µL to 100 ng/µL.
[2] Linear function $Y = bX + a$, where the coefficients b and a are called "slope" and "intersection," respectively, is called "linear" because it makes a straight line when it is graphed.

the range of 'working' concentrations of PE from 0.05 ng/μL to 4 ng/μL, the relationship "normalized PE peak area (*Y*) – PE concentration (*X*)" is far from being a directly proportional one, and instead, based on the Gaudreau and Brazeau's experimental data, the relationship "$Y - X$" was approximated by the following liner regression equation (see Eq. 1 above):

$$Y = 25500\,X - 2283 \qquad \text{(Eq. 3)},$$

where the above coefficient ("intersection") *a* is equal to minus 2283, i.e. the coefficient *a* is evidently significantly different from zero [2, Appendix 3].

Finally, Table 1 also shows that practically all the numerical data (normalized peak areas of PE) obtained for each of the four standard solutions of PE, as well as the directly proportional relationship "normalized peak area of PE (*Y*) – PE concentration (*X*)," remained virtually unchanged after all maintenance procedures done to the GC-MS instrument, such as "*maintenance to the injector, which included changing of the septum and liner, as well as removing a portion of the leading edge of the column, and after maintenance to the source, which included removal of a portion of the end of the column*."

Based on the above-mentioned, the data in Table 1 is dubious. Moreover, even if one were to assume that *1)* Lyter not only was lucky to obtain a very atypical for GC-MS directly proportional relationship "signal – concentration," but *2)* in addition to that, this directly proportional relationship remained virtually unchanged first after the "*maintenance to the injector, which included changing of the septum and liner, as well as removing a portion of the leading edge of the column,*" and then after the "*maintenance to the source, which included removal of a portion of the end of the column,*" it would still be scientifically unsound to conclude that "*cleanliness of the instrument has [no] impact upon the … ability [of GC-MS] to accurately and precisely measure the quantity of semi-volatile components [such as PE].*"

Such a conclusion contradicts numerous scientific publications addressing the problems of the GC analysis of polar compounds and specifically organic compounds with polar hydroxyl groups, such as PE and similar high-boiling solvents. In GC, these polar compounds are considered active analytes that can be difficult to chromatograph because they are susceptible to adsorption onto active surfaces in the sample flow path, including the GC column itself. For this reason, the peaks for these compounds tend to tail when there are active sites along the GC flow path, which makes it hard to determine accurate peak areas and therefore may severely compromise results of their quantitative analysis. To avoid problems with PE peak tailing, which may lead to partial loss of PE and thus to inaccurate results of its quantification by GC-MS, multiple researchers [3-9] recommended derivatization (silanization) of PE prior to its GC analysis in order to create a non-polar derivative of PE (e.g., trimethylsilyl-PE) that is not susceptible to adsorption onto active surfaces in the sample flow path. If PE is analyzed by GC-MS without its prior derivatization, then Gaudreau and Aginsky [1] recommended *1)* that the GC-MS instrument (specifically, the injector, the liner, the GC column, and the MS detector) should be clean and inert enough to avoid or at least minimize the amount of active surfaces in the sample flow path and therefore to provide reliable quantification for both PE (extracted from ink on paper sampled from the document) and the internal standard used, and *2*) that the most effective way to ensure that the GC-MS instrument is clean and inert enough to provide reliable quantification of PE is if the GC-MS system is devoted for ink analysis only. They clarified that if the GC-MS instrument "also used for the analysis of other materials [including materials] of forensic interest, for example, drugs of abuse, toxic substances, fire debris, and/or explosives residues, then the GC-MS system will be inevitably contaminated by these materials and products of their decomposition that will create numerous active sites in the sample flow path and thus will render reliable quantification for PE and the internal standard impossible" [1].

In addition to contradicting numerous scientific publications addressing the problems of the GC analysis of polar compounds (as discussed above), Lyter's conclusion that "*cleanliness of the instrument has [no] impact upon the … ability [of GC-MS] to accurately and precisely measure the quantity of semi-volatile components [such as PE]*" cannot be scientifically sound for the obvious reason: when an analyst uses a GC-MS instrument that is not dedicated to one type of analysis, e.g., the analysis of ink on documents, but is instead used for analysis of various substances (the case that is apparently implied by Lyter in the Technical Note), the analyst has no idea whether, at a given point in time, the instrument is (Scenario 1) or is not (Scenario 2) clean

and inert enough "*to accurately and precisely measure the quantity of [polar] components [such as PE].*"

Having this in mind, it is still possible that the GC-MS instrument used by Lyter to obtain the data listed in Table 1 could be classified under Scenario 1, i.e. the GC-MS instrument proved to be clean and inert for analyzing polar compounds before Lyter conducted the above mentioned "*maintenance procedures.*" For instance, such a scenario is plausible if *A)* before the GC-MS instrument was used by Lyter, another analyst had done some maintenance to the instrument, e.g. installed a fresh column and changed the septum and liner, or *B)* the GC-MS analyses that had been conducted by that analyst did not involve substances that could sufficiently contaminate the column and/or other parts of the instrument and thus did not create active sites along the GC flow path.

2. Scope of Applicability of the Solvent Loss Ratio Method is about six months

The Solvent Loss Ratio Method (SLRM) is the ink aging method that determines the rate, *R%*, at which the volatile component (PE or a similar high-boiling solvent) content of ink decreases at the time when the ink is being examined. This method (first reported as *Rate of decrease of volatile components R%* in my 1996 article "*Dating and Characterizing Writing, Stamp Pad and Jet Printer Inks by Gas Chromatography/Mass Spectrometry*" [10-12[3]] and then further described in two papers in 2002 [2] and 2010 [1]) is routinely used by the Forensic Sciences Division of the Canada Border Services Agency (CBSA) (former Canada Customs and Revenue Agency, Ottawa, Ontario, Canada) for determining the approximate age of ballpoint ink on paper (in cases when there is a possibility that the age of the ink can be *less than 6 months* [13]).

Recently, multiple ink chemists in various countries have studied aging processes occurring in ballpoint ink on paper, including the "*decrease in the level of PE*" during both natural aging (at room temperatures) and artificial aging. The artificial aging is used as one of the stages of the SLRM (ink samples are heated at 70 degrees Celsius, and then the difference between the levels of PE in the unheated and heated ink samples is measured by GC-MS and the result obtained is used to calculate the ink aging parameter, *R%*). The results of these studies (in total, hundreds different inks have been tested) have shown that the *gradual loss with time of the high boiling solvents* contained in ink on paper can typically correlate with the actual age of ink within only first several months after the ink was placed on paper. Multiple articles and conference papers that report the results of these studies are discussed in recent publications [14-17]. Based on all experimental data published in both peer-reviewed articles and conference papers, it is now generally accepted that the scope of applicability of the SLRM does not allow one to use the method for dating ballpoint inks older than six (6) months, because the ink aging parameter *R%* correlates with the actual age of ink only for no longer than six (6) months after the ink was placed on paper.

In the above Technical Note, Lyter discussed the solvent loss ratio (SLR) data obtained for one blue ballpoint ink entry and one black ballpoint ink entry (both prepared in April of 2018) the "age" of which (at the moment of their examination in June of 2018) was not more than three months and claimed that, for the inks of such a young age, *"[o]ne would expect the examination results of the SLR method to be either greater than 50, an indication of preparation date within 6 months of the examination date, or greater than 35, an indication of preparation date within 18 months of the examination date.*"

When stating that if the ink aging parameter *R%*, which is measured by SLRM, is "*greater than 35[%] [then this is] an indication of preparation date within 18 months of the examination date,*" Lyter relied on the 2010 conference paper [1] in which Gaudreau and Aginsky substituted the earlier used 25% threshold (initially reported by Gaudreau and Brazeau as the threshold that they believed would allow one to determine whether an ink on paper is younger than 10 months [2]) with a new, "revised" 35% threshold that, based on a number of experimental data obtained by the Forensic Sciences Division of the CBSA, looked suitable to be used to determine whether an ink on paper is younger than 18 months [1].

Later, however, the analysis of an extensive set of experimental data (totaling 286 *R%* values),

[3] In 2017, Cantu referred to this ink-aging method as "*the solvent loss ratio method (SLRM) of Aginsky*" and mentioned it as one of the "*four methods to estimate the age of an ink [that] are the major ones based on the analysis of ink solvents*" [12].

obtained by the CBSA laboratory by 2010 when examining ballpoint inks of various formulations using SLRM, showed that numerous false-positive results were obtained not only for the old (and already not used) 25% threshold, but also for the new, "revised" 35% threshold. The analysis of the 286 *R*% values clearly shows that the 35% threshold proved to be completely unacceptable for its use in the SLRM [14-16].

As I am aware, at present, the CBSA laboratory is relying on only one "threshold" when using the SLRM – *R=50%:* if the value of *R*% is statistically significantly larger than *50%*, then it indicates that the age of the ink is less than six (6) months [13]. That is, the CBSA laboratory has agreed with what is now generally accepted, namely, that the scope of applicability of the SLRM does not allow one to use the method for dating inks older than six (6) months.

Summing it up, it is now generally accepted by the overwhelming majority of the pertinent scientific community that the ink aging parameter *R*% that is measured by the SLRM correlates with the actual age of ink only for no longer than six (6) months after the ink was placed on paper.

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