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Analysis of Phenoxyethanol: Instrumental Parameters and Effects

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In the last 10 to 15 years several examination methodologies have been proposed that rely on the quantitative analysis of semi-volatile components in writing ink, such as Phenoxyethanol (PE), for the purpose of determining the date of production of the writing. These examination methodologies require the use of analytical instrumentation that is capable of determining with great sensitivity and specificity both the identity and quantity of these components. The instrumentation of choice is gas chromatography/mass spectrometry (GC/MS) with the sample introduction methods varying from solvent injection to thermal desorption.

This work addresses the impact that various instrumental conditions and parameters will have on the ability to accurately and precisely measure the quantity of semi-volatile components. Instrumental components ranging from the injector, through the column, to the source were evaluated by sequential analysis of a range of standard solutions, both before and after maintenance procedures. Since most of the examination methodologies involve the comparison of writing ink samples both with and without exposure to artificial aging conditions, such samples were also included in the examination scheme.

Analysis of the above referenced samples resulted in an effective evaluation of the extent to which any instrumental parameter affects the ability to accurately determine the amount of semi-volatile components present in a writing ink sample. Linear relationships were determined between standard solutions of varying concentrations and among writing ink samples of varying concentrations. The condition of instrumental components was found to have a minimal, measurable effect upon quantitative determinations of the concentration of semi-volatile components. Ultimately, the comparison of writing ink samples with artificially aged samples was found to produce data that was capable of reliably determining the age of the examined writings and was not affected by the instrumental parameters that were tested.

Introduction

The use of gas chromatography – mass spectrometry (GC/MS) in the examination of writing inks for the purpose of determining the age of the writing has presented a powerful tool but has also raised numerous questions. [1-7] GC/MS is recognized throughout science as a useful and practical methodology for the analysis of volatile components. GC/MS is used routinely in forensic science to analyze toxicological samples, fire debris samples and illicit drugs. In each of these areas it was necessary to determine the limitations of GC/MS as it related to the particular analysis at hand.

GC/MS is a methodology that relies upon the interaction of a sample with the coating on a column over a range of temperatures. It is the ability to change and control temperature accurately that provides for the range of analyses that are possible. This range of useful temperature, however, also results in the deposition of material on various portions of the instrument. These materials can have a deleterious effect on the analysis, which is why it is normal practice to access this effect and perform the appropriate routine maintenance. In order to access the effects of the deposition of materials will have on an examination methodology for the determination of the age of writing ink, an investigation was undertaken that performed routine analysis of writing ink by GC/MS both before and after the performance of routine maintenance.

Methods and Materials

The GC/MS used in this investigation was an Agilent Model 6890N Gas Chromatograph coupled

with an Agilent Model 5975B Mass Selective Detector. The column used was an Agilent HP5-MS, 30 meters, 0.25mm ID and 0.25µm film and the carrier gas was helium. Samples of PaperMate® blue and black ball pen ink were prepared by the author by writing on copy paper. Samples were removed from these papers with a 0.5mm diameter Harris Punch and inserted into vials containing 200µl inserts. LCMS grade Acetonitrile (Fisher Scientific) was used for the preparation of standard phenoxyethanol (Sigma Aldrich) solutions, and for extraction of ink samples. Cresol (Sigma Aldrich) was used as the internal standard for all ink samples. Artificially aged ink samples were prepared by heating for 2 hours at 70° C.

The GC/MS method required an injection of 1µl of the sample of interest. Samples were injected manually, unless otherwise noted. The initial temperature was 75° C, which was held for 1.5 minutes, and the temperature was ramped to 250° C at 25° /min. The final temperature was held until 16.5 minutes had elapsed. The injector temperature was 250, the transfer line was 230° and the carrier gas flow rate was 1ml/min. The mass spectrometer was set in positive EI and full scan mode between 50 and 400amu. It was engaged/online from 3 minutes until 13 minutes during the run.

The described GC/MS was used in the performance of listed analyses on three different occasions: initially prior to any maintenance, after 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.

A series of PE standard solutions, (0.1, 1.0, 10 and 100 ng/µl) were analyzed using the above GC/MS methodology. This occurred initially prior to any maintenance, and then again after each maintenance procedure.

Multiple samples (5) from each of the PaperMate® writings were analyzed for the presence and quantitation of PE. Both neat samples and artificially aged samples were examined. The samples were made of 6 µplugs and the extraction volume was 5µl of acetonitrile with internal standard. The date of preparation of the writings was April 2018. The methodology used for this examination was the SLR method. [4-5]

Results and Discussion

The results of the analysis of the PE standard solutions are listed in the following table. These values were generated by dividing the integrated peak area for the PE standard with the integrated peak area for the 100ng standard. Note the consistency both before and after maintenance indicating that the cleanliness of the instrument was ineffectual regarding the quantitation of PE.

The following table illustrates the average SLR's for both the blue PaperMate® writings and the black PaperMate® writings. In several measurements the SLR was a negative number. As described in the literature this is due to the SLR not being a mass independent measurement, with the quantity of ink in individual samples found to vary. [7] The examination procedure is designed to minimize this factor by instructing the examiner to remove samples in close proximity to each other. [4-5]

The examined writings were prepared in April of 2018 and the examinations were performed in June of 2018. One 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

Table 1. Normalized quantitation of PE in standard solution.

Samples	0.1 ng/µl	1 ng/µl	10 ng/µl	100 ng/µl
Before Maintenance	0.001	0.01	0.10	1.0
Injector Maintenance	0.001	0.01	0.09	1.0
Source Maintenance	0.001	0.01	0.09	1.0

Table 2. Average Solvent Loss Ratio of PaperMate® ink writings during maintenance cycle.

Samples	Before Maintenance	Injector Maintenance	Source Maintenance
PaperMate blue®	56	31	42.7
PaperMate black®	37.4	30	26.7

months of the examination date. It is clear from the data in this table that the level of cleanliness of the instrument is not the overriding factor in assessing the date of preparation of writing using this examination methodology. The presence of negative SLR's impacts any set of data and makes a good argument for the inclusion of multiple samples when this procedure is employed.

Conclusion

The ability to reproduce a consistent relationship between multiple samples of PE standard solutions both before and after various routine maintenance procedures is demonstrated. This would indicate that any variability found in the measurement of PE is due to either the complexity of the ink in which the PE is found, or the performance of the examination methodology. It does not suggest that the cleanliness of the instrument has any impact upon these measurements. Any impact of the instrument cleanliness would involve any examination sequence, no matter the nature of the samples being examined.

The data generated regarding the examination of multiple samples of two different ink formulations illustrate the issues that must be addressed in performing the SLR Method. Precise sampling of a writing and the use of multiple samples in the examination of writings are two areas that require attention by an examiner performing this method.

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