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Bank Security Dye Packs: Synthesis, Isolation, and Characterization of Chlorinated Products of Bleached 1-(methylamino)anthraquinone

ABSTRACT: Banknote evidence is often submitted after a suspect has attempted to disguise or remove red dye stain that has been released because of an anti-theft device that activates after banknotes have been unlawfully removed from bank premises. Three chlorinated compounds have been synthesized as forensic chemical standards to indicate bank security dye bleaching as a suspect's intentional method for masking a robbery involving dye pack release on banknotes. A novel, facile synthetic method to provide three chlorinated derivatives of 1-(methylamino)anthraquinone (MAAQ) is presented. The synthetic route involved Ultra Clorox™ bleach as the chlorine source, iron chloride as the catalyst, and MAAQ as the starting material and resulted in a three-component product mixture. Two mono-chlorinated isomers (2-chloro-1-(methylamino)anthraquinone and 4-chloro-1-(methylamino)anthraquinone) and one di-chlorinated compound (2,4-dichloro-1-(methylamino)anthraquinone) of the MAAQ parent molecule were detected by gas chromatography mass spectrometry (GC-MS), and subsequently isolated by liquid chromatography (LC) with postcolumn fraction collection. Although GC-MS is sensitive enough to detect all of the chlorinated products, it is not definitive enough to identify the structural isomers. Liquid-state nuclear magnetic resonance (NMR) spectroscopy was utilized to elucidate structurally the ortho- and para-mono-chlorinated isomers once enough material was properly isolated. A reaction mechanism involving iron is proposed to explain the presence of chlorinated MAAQ species on stolen banknotes after attempted bleaching.

KEYWORDS: forensic science, forensic chemistry, theft-deterrent device, dye pack, dye bleaching, chlorinated derivatives, MAAQ, bank security, bank dye, bank robbery, stained currency, security inks

Bank security dye packs are theft-deterrent devices that attempt to render stolen currency unusable. Only a few companies have been involved in dye pack production from the first device conception developed in the 1970s. Manufacturers such as U.S. Currency Protection Corporation (1,2) and 3SI Security Systems (3–7) have been the major bank security dye pack suppliers for years. Recently, 3SI acquired U.S. Currency Protection Corporation's production and dye pack distribution, and is now reportedly the major United States security device supplier (8).

There are multiple purposes for dye packs. The major deterrence of bank robberies relies on all stolen banknotes becoming worthless upon dye pack deployment. Attempts to stain all stolen money once it is illegally removed from the bank to render it nontransferable are another reason why banks and insurance companies (e.g., Federal Deposit Insurance Corporation) encourage security pack use. Law enforcement personnel benefit from the use of a red smoke because such smoke typically draws attention to both the crime and the fleeing suspects. Contamination of other materials (e.g., clothes, skin, and vehicles) from the dye aids with investigative leads by possibly linking a crime to a suspect. While the dye itself cannot match a suspect to an individual bank or dye pack, evidence from other forensic disciplines (e.g., DNA, fingerprints, and trace evidence) can be used in conjunction with the presence of red-stained currency to support an investigation.

The red chemical is 1-(methylamino)anthraquinone (MAAQ) and the chemical structure is depicted in Fig. 1. MAAQ is usually mixed with oxidizing material, a fuel, and other chemicals to form the smoke mix packaged in security packs. When ignited, this mixture produces both red smoke and intense heat. The dye packs are remotely activated once they are removed from the bank premises. The chemical smoke mixture tends to adhere irreversibly to many materials (e.g., clothing, skin, footwear, automobile carpet, and tote bags). MAAQ has unique chromophoric properties that allow the smallest amount to be observed with the unaided eye. MAAQ is also insoluble in many common solvents (e.g., water), so attempts to rinse off the red stain are difficult. Additionally, further deterrents such as tear gas [e.g., α chlorobenzylidene malononitrile (CS), chloroacetophenone (CN)] are added to either the smoke formulation or the dye packs. From a forensic perspective, the presence or absence of a lachrymator, in conjunction with the MAAQ dye, can be of significant importance in a criminal investigation.

In an attempt to render stained currency useful, or in order to remove the red color from other evidentiary material, suspects have occasionally attempted to use bleach on stained items. Bleach, sodium hypochlorite (NaOCl), has been known to oxidize other chemicals and cause disruption in the conjugation of chromophores. An example is bleach addition to an aqueous crystal violet solution, a common purple dye used in blue and black ballpoint pen ink formulations, which causes the solution to turn colorless in seconds. Thus, if successful with MAAQ, bleach

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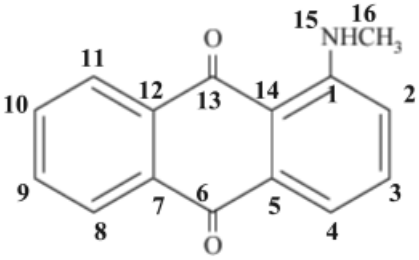


FIG. 1—*The chemical structure of 1-(methylamino)anthraquinone depicts the stable three-fused ring aromatic system. Single chlorination occurs via a substitution reaction at the ortho- or para-positions relative to the methylamino substituent. The numbers in the figure label positions for unequivalent protons that will be referenced for ^1H NMR resonances in Fig. 7.*

could theoretically eliminate the red stain from currency and other evidentiary material. It would be beneficial to understand chemically what is occurring to the MAAQ once exposed to bleach so that attempts at identifying possible by-products can be performed for forensic purposes. Fortunately, for crime investigators, bleach does not completely remove red MAAQ stains from materials commonly related to bank robberies (e.g., currency, clothing, bags).

Owing to the anthraquinone's fused three-ring system, the molecule is extremely stable and difficult to oxidize. The concept of using a chlorinated oxidizing agent (i.e., bleach) to oxidize conjugation within the MAAQ molecule, and thus cause disruption in its chromophoric ability, is not uncommon. Instead of removing the red stain from evidentiary items, bleaching tends to lighten red stains to a pinkish hue, while at the same time dispersing the color into unstained areas. Physical changes can occur to the evidentiary items such as whitening of paper products (i.e., currency), fading of other dyes, smelling of chlorine, and/or deteriorating of the actual evidence.

The forensic examination of security dye pack evidence usually involves four (4) steps:

(i) stain visualization;
(ii) dye extraction with a solvent;
(iii) thin-layer chromatography (TLC); and
(iv) gas chromatography/mass spectrometry (GC-MS).

Owing to MAAQ's ability to absorb light at low dye concentrations, it is unlikely that MAAQ is present at analytically detectable levels if a red color is not visualized on an item. It is also difficult to sample evidence that does not visually indicate a red color because the forensic examiner would not know where to sample. When a red stain is observed, stain extraction is performed with an organic solvent such as methanol or chloroform. If solvent extraction does not result in a reddish solution, then MAAQ probably is not present. If a pink or red solution is obtained from the extraction process, TLC can efficiently and effectively differentiate many red dyes from MAAQ (9). Sometimes, if extracts are heavily contaminated with chlorinated MAAQ derivative compounds, multiple bands on the TLC plate may appear. There are other materials that have utilized this dye, most notably red automobile taillight lenses, but MAAQ presence on banknotes is considered unlikely unless exposed to bank security device deployment. GC-MS is used as a confirmatory technique to identify the bank dye components: MAAQ and tear gas (if present). Different mass spectral parameters have been compared in order to determine the most sensitive spectral technique (e.g., electron impact vs. chemical ionization, and negative chemical ionization vs. positive chemical ionization) (10).

When a chlorinated oxidizing agent such as bleach is used on stained MAAQ items, the resulting stain can become significantly faded and pink in color. After this faded stain has been visualized and extracted into solution, the results from GC-MS analyses often reveal the presence of three peaks in addition to the MAAQ compound. These peaks are consistent with chlorine-related MAAQ compounds based on the isotopic abundances of the mass-to-charge ratios (*m/z*) of each peak's mass spectrum. Forensic examiners routinely use the phrase, "consistent with" when reporting results on the chlorinated MAAQ compounds, because no chemical standards have been commercially available to use as positive controls for comparison purposes. Once the chlorinated MAAQ compounds are isolated and characterized, other information such as how NaOCl and MAAQ react under varying conditions can be pursued.

Research presented in this manuscript focused on two objectives: (1) the preparation of chemical standards representing the possible chlorinated products of MAAQ bleaching and (2) the identification of the reaction mechanism involved when criminals attempt dye obliteration from currency. One chlorinated reaction product has already been synthesized and described by an American Cyanamid patent (11). Complex organic chemical reactions described in the patent: (1) are highly unlikely in criminal cases involving bank currency and (2) the relatively low experimental yields for the disclosed reactions do not make this pathway an easy synthetic route. Instead, a simple experimental approach involving chemicals that are typically available to criminals was investigated. This approach led to the discovery of a synthetic route in solution for a mixture of possible chlorinated MAAQ products.

Product isolation and structural characterization to provide pure compounds that could be documented and utilized as standards in casework were also undertaken in this work. A liquid chromatography (LC) method described elsewhere (12) was modified to quickly collect chlorinated MAAQ product fractions over a short time interval. Structural characterization of the two mono-chlorinated isomers for correct fraction assignment was performed after sufficient material was collected for chemical standards. Liquid-state nuclear magnetic resonance (NMR) was performed to identify the correct isomer with the correct fraction. Finally, a reaction mechanism is suggested to explain why chlorinated products occur in criminal cases despite the seemingly low probability of chlorine substitution when a catalyst is absent.

Methods

Synthesis

A chlorinated MAAQ mixture was prepared in an Erlenmeyer flask with 5.0 mg of MAAQ (Aldrich, St. Louis, MO, 98%) in 5.0 mL methanol (Fisher Scientific, Hampton, NH). The reaction catalyst, 20.0 mg of $FeCl_3 \cdot 6H_2O$ (Fisher Scientific), was added to the methanol. Substitution reactions were initiated with 700 µL of Ultra Clorox™ (Oakland, CA) bleach (7% w/v NaOCl). Bleach addition caused a precipitate that indicated immediate reaction. After settling, the supernatant was filtered through a 0.2 µm nylon syringe filter (Nalgene, West Chester, PA).

TLC

A qualitative method to differentiate MAAQ from other red dyes, and observe potential chlorinated derivatives of MAAQ, is TLC. TLC is the preliminary step that a scientist uses when

analyzing evidence for bank dye. Evidence in bank robbery cases is not limited to currency. Evidence can include materials such as bags used to tote currency (e.g., plastic and duffle bags), clothing, and automobile carpet. Methanol or chloroform solvent extraction is performed to remove potential MAAQ from evidence. A spot of extracted material was applied to a 10 × 10 cm Partisil LHP-KF TLC plate (Whatman, West Chester, PA) with a 200 μm thickness silica layer and 60 Å pore size. The extraction solvent was allowed to evaporate. MAAQ positive control was also spotted on the TLC plate as a reference standard. The TLC solvent was 100% toluene (Fisher Scientific), and 15 min of development time was allowed before the plate was removed and dried. MAAQ is a red band visualized on the TLC plate by the unaided eye. Potential chlorinated compounds were indicated by a light pink spot possessing a larger R_f when compared with the MAAQ standard, due to the larger distance traversed on the TLC plate.

GC-MS

GC-MS methods implemented for MAAQ mixture analysis have been previously described (10) and were adapted from the Chemistry Unit standard operating procedure (SOP) for suspected bank dye evidence. An Agilent 6890N GC oven (Santa Clara, PA) with an Agilent 5973 MSD was utilized for separations involving MAAQ and chlorinated MAAQ reaction mixtures. The GC and MSD instruments were controlled by MSD ChemStation software. A 30 m length, 0.25 mm internal diameter DB5-MS column (Agilent Technologies) with 0.25 μm stationary phase film thickness was utilized. The injection port and mass spectrometer transfer line temperatures were 250°C and 280°C, respectively. The initial GC oven temperature was 60°C and held for 2.0 min after sample injection. The programed temperature ramp rate was 35°C/min until a final temperature of 260°C was attained and held for 10 min, resulting in a total run time of 17.71 min. Helium carrier gas flow was held constant at 0.9 mL/min. Reaction mixtures were injected having 1 μL volumes with a 10:1 injection split ratio. Electron impact (EI) ionization mode was utilized with mass range scanned from *m/z* 50 to 500 at a 1.68 scans/sec data rate after a 3-min solvent delay. For chemical purity determination, a 5 μL injection of individual LC fractions was utilized to obtain the results presented in Fig. 6.

LC

A Waters Alliance HT 2695 LC system (Milford, MA) with a Waters 486 tunable absorption detector set at 254 nm was utilized for the LC separation of the postreacted mixture. LC protocols were adjusted from those developed for tear gas and bank dye detection (12). The column was a 4.6 × 150 mm Zorbax Eclipse XDB-C8 (VWR International, West Chester, PA) with 5 μm particles. The mobile phase consisted of a gradient program starting with 50:50 methanol:water and ending at 80:20 methanol:water after 5 min. The mobile phase flow rate was held constant at 1 mL/min over the entire 15 min experimental time. Empower software was utilized to externally control the liquid pumping and detector systems. The detector outlet was configured to deliver solution to an Advantec SF-2120 Super Fraction Collector postdetection (VWR International, West Chester, PA). The programed fraction collector dispensed 1 min intervals into four separate vials to collect unreacted MAAQ and pure chlorinated isolates. The collected fractions were summed, evaporated, and redissolved before injection into the GC-MS system described above to verify purity.

Liquid-State NMR

A Bruker 400 MHz (9.4 T) magnet operating with XWINNMR software (version 3.0) was used to collect ^{1}H NMR spectra of reaction product fractions. All samples were dissolved in 0.5 mL $CDCl_3$. Shimming was performed on deuterium lock signal. A single 13 μsec excitation pulse at 400.1324710 MHz was utilized for protons. Chemical shifts were referenced to an internal TMS resonance. Sample signal averaging for 2048 scans with 3.9 sec acquisition times resulted in 3 h experiments. Signal processing involved Fourier transformation with slight zero- and first-order phase corrections and without line broadening. Preliminary signal-to-noise (S/N) experiments on a 2 mg MAAQ sample were performed with adequate sensitivity after 16 scans and resulted in less than 1 min acquisition times. Initial S/N measurements determined the data acquisition feasibility for collected fractions consisting of approximately 100 μg.

Micro X-Ray Fluorescence (μ-XRF) and Scanning Electron Microscopy

Elemental image analysis was performed to provide insight on uncatalyzed bleach reactions of MAAQ on US paper currency. An EDAX Eagle II polycapillary spectrometer μ-XRF (Mahwah, NJ) equipped with a rhodium tube and a Varispot spot size control collected low-magnification images and produced elemental maps for qualitative association of selected elements with the dollar bill inks. A one-dollar bill was placed under vacuum, and the maps were collected using a tube voltage of 16 kV and a current of 360 μA with a 17 μsec time constant. Elemental maps were collected using × 10 magnification, with 256 × 200 point matrices and dwell times of 500 msec on each point. The sampling spot size was set to ~ 40μm, and there was no overlap between collection points of the selected matrix size.

The scanning electron microscope (SEM) provided complementary information to the μ-XRF images with higher magnifications. A LEO-1450VP SEM (New York, NY) with an EDAX energy-dispersive spectrometer (EDS) was used to collect images and produce qualitative elemental maps. The SEM was operated in variable pressure mode (25 Pa) to reduce charging and eliminate the necessity for a conductive coating. Images and maps were collected at 20 kV with a probe current of 1 nA.

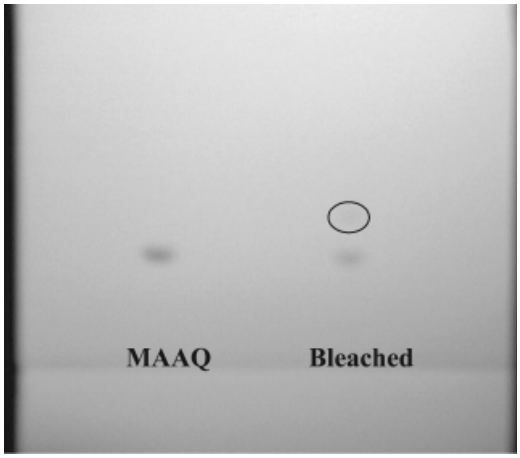
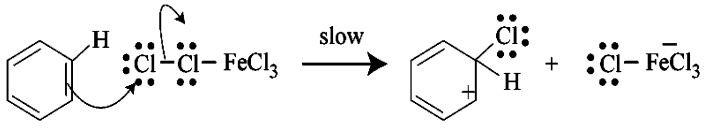


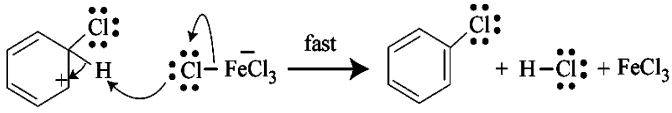
FIG. 2—*Thin-layer chromatography plate was developed with two separate solutions spotted side by side. On the left is the 1-(methylamino)anthraquinone (MAAQ) standard at 1 mg/mL and on the right is the reaction mixture after bleaching. The circle indicates the presence of a faint pink band that represents chlorinated reaction products.*

Results and Discussion

Chlorinated MAAQ compound synthesis must be simple, rapid, and of high yield to produce in-house chemical forensic standards. Iron chloride ($FeCl_3$) is the catalyst that is necessary for significant chlorine substitution to occur on an aryl ring (13). The following mechanism has been proposed for similar hydrogen–halogen substitution reactions:



[1](13)



[2](13)

$FeCl_3$ was added to a room-temperature MAAQ solution and bleach provided the chlorine source necessary for reaction. Once the reaction had occurred and the precipitate settled, the supernatant was removed, filtered, and evaporated to prevent further bleaching. If the reaction was allowed to continue, a colorless solution was eventually observed as a result of substantial structural damage to the MAAQ-conjugated ring system. No chlorination or color loss was observed at room temperature if the catalyst was absent from the reaction solution. Iron can also be utilized for the chlorination reaction but must first react with chlorine to produce the weak Lewis acid, $FeCl_3$ (13).

TLC and GC Analysis of Reaction Mixture

TLC was the preliminary test used to observe chlorinated MAAQ species. Figure 2 shows a digital photograph of the TLC results from the reaction mixture after a 15-min development with 100% toluene. Two faint pink-colored spots were observed. The darker red spot corresponds to MAAQ as demonstrated by the MAAQ chemical standard run alongside the mixture. The circled pink spot that migrates further up the TLC slide is sometimes observed when banknotes have been suspected of being bleached. TLC is not capable of further resolving the various reaction products encountered when evidence has been bleached.

GC-MS was performed to determine the presence of reaction products, extent of reaction, and percent yield. Figure 3 depicts the total-ion count chromatogram for the reaction mixture. Four peaks are labeled with the retention time and correspond to the unreacted MAAQ (10.58 ± 0.01 min), mono-chlorinated MAAQ (11.30 ± 0.01 min), a second mono-chlorinated MAAQ isomer (13.12 ± 0.02 min), and a di-chlorinated MAAQ compound (13.80 ± 0.02 min). Figure 4 contains mass spectra obtained for each individual chromatographic peak with the retention time displayed on the right. MAAQ displays *m/z* 237 and a minor fragment peak at *m/z* 220. Both mono-chlorinated isomers contain *m/z* 271 due to the chlorine substitution reaction and the 3:1 isotopic ratio corroborates this assignment. Each isomer also contains another peak at *m/z* 254 due to the same mass loss (-17 Da) observed for the MAAQ parent molecule, but the ratio of this peak to the molecular ion (*m/z* 271) differs between isomers. Di-chlorinated MAAQ contains *m/z* 305 due to double chlorine substitution and a peak at *m/z* 288 due to the -17 Da mass fragment. The percentage of each reaction product was estimated by peak area relative to each other and resulted in 1.7% unreacted MAAQ, 29.0% mono-chlorinated isomer I, 59.2% mono-chlorinated isomer II, and 10.1% di-chlorinated MAAQ.

Chlorine substitution of the mono-chlorinated isomers is dependent upon the aryl ring substituent effects. Methylamino groups (NHR) are considered strongly activating groups and direct substitution occurs at the para- or ortho-aryl ring positions of the methylamino-bearing MAAQ ring. Isomeric compound percentage yields are not discriminate enough to determine chemical identity because it is difficult to predict the ortho/para product ratio (14). Too many reaction conditions affect the substitution site, including attacking group steric hindrance, reaction temperature, and parent molecule steric hindrance. Based on gas chromatographic arguments with the nonpolar stationary phase, the first eluted mono-chlorinated species (11.30 min) is tentatively assigned to the ortho isomer because it is more polar than the para isomer. MAAQ di-chlorination was not expected because single chlorination introduces a deactivating group (meta-directing) into the aryl ring. However, both the NHR and halogen substituents direct further substitution to the same aryl ring position and therefore di-chlorination is strengthened for that position (14).

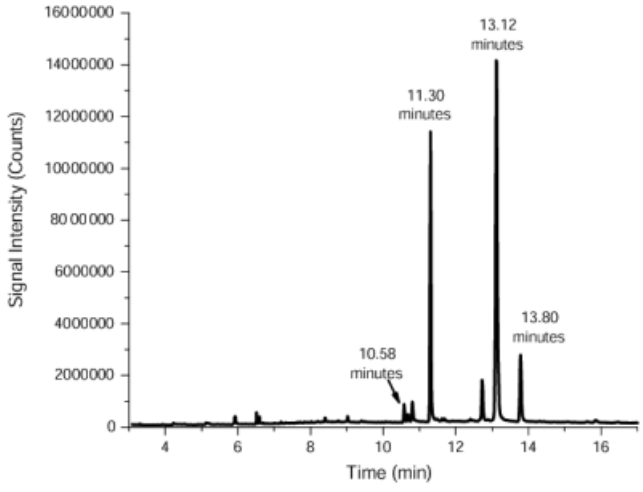


FIG. 3—*Total ion count gas chromatogram for the mixture after catalyzed bleach reaction displays the unreacted 1-(methylamino)anthraquinone compound (10.58 min) and three reaction products: two mono-chlorinated isomers (11.30 and 13.12 min) and a di-chlorinated product (13.80 min).*

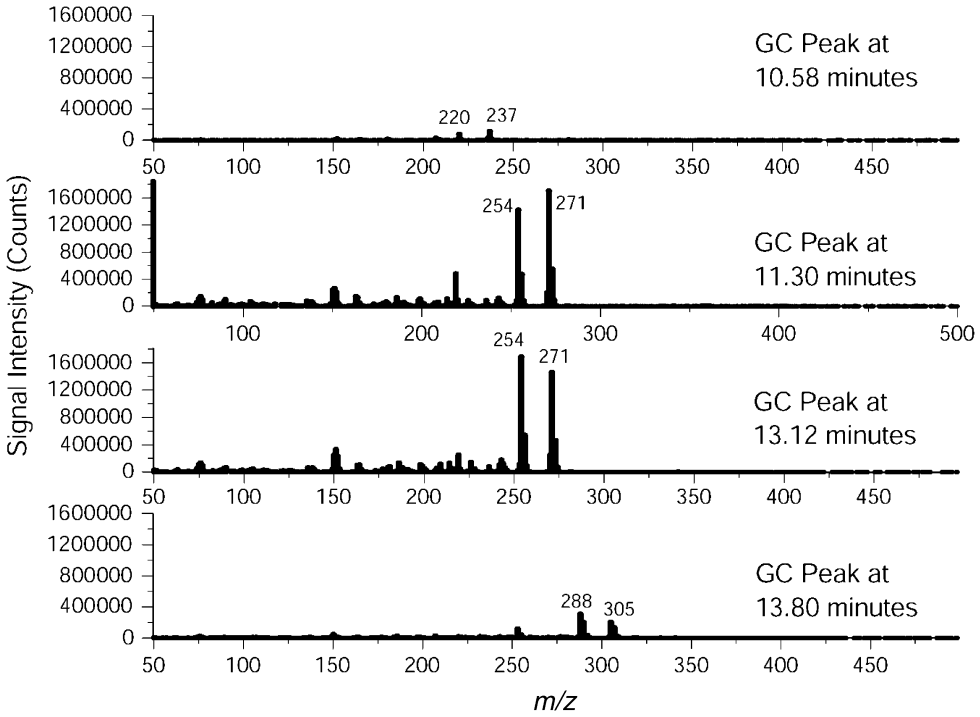


FIG. 4—*Individual mass spectra at the maximum chromatographic peak heights indicate the presence of two mono-chlorinated isomeric compounds and one di-chlorinated compound.*

LC Fraction Collection

LC was performed to isolate each individual component for NMR analysis. Figure 5 represents the chromatogram recorded at 254 nm with a 10 μL sample mixture injection. Four peaks are labeled with retention times and correspond with the reaction products detected in GC. The elution order for the mono-chlorinated species was different from those observed in GC: unreacted MAAQ at 8.01 ± 0.04 min, mono-chlorinated MAAQ products at 8.24 ± 0.05 min and 10.94 ± 0.10 min, and the di-chlorinated MAAQ product at 11.79 ± 0.11 min. Minor peaks present in the chromatograms were probably due to bleach degradation products. After a single fraction was collected, the mobile phase was evaporated and the sample was redissolved in 20 μL of methanol. A GC-MS sample injection of each product fraction was performed to validate the collection pro-

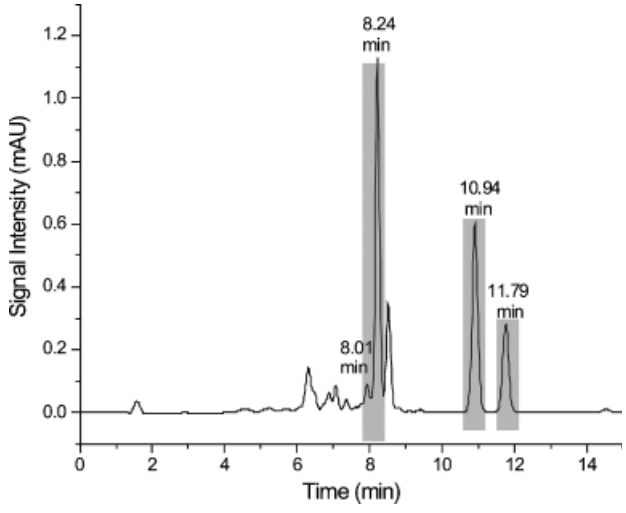


FIG. 5—*Liquid chromatogram detected at 254 nm for the reaction mixture indicated a change in elution order between the two mono-chlorinated isomers. The shaded areas highlight the times used for individual fraction collection.*

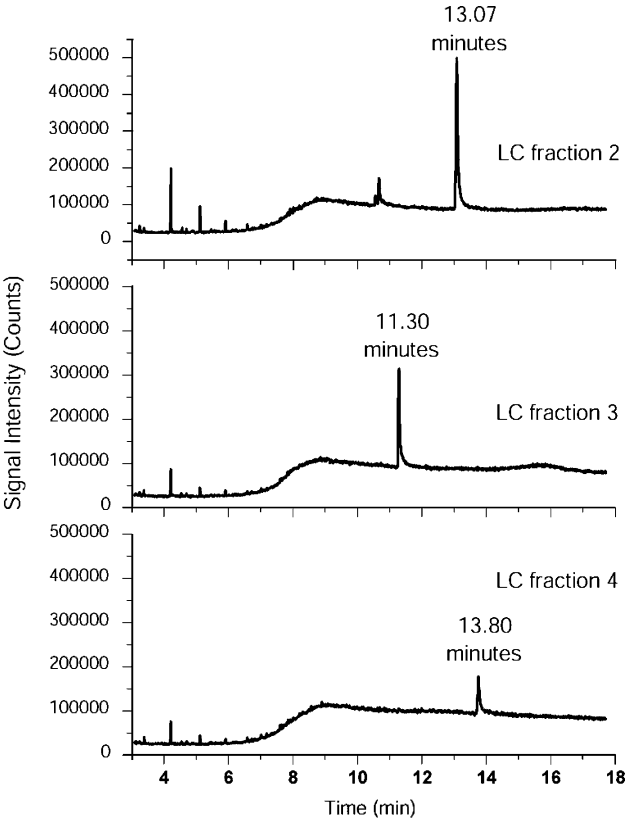


FIG. 6—*Total ion gas chromatograms for each reaction product composed of 100 individual fractions collected in the liquid chromatography (LC) experiments. Mass spectra are not included but correspond to those contained in Fig. 4.*

cedure and confirm peak assignment. The highlighted chromatographic regions correspond to the fraction times that were collected for each peak. One hundred fractions of each time window were collected for both further structural characterization and chemical standard preparation. It was determined that the mono-chlorinated isomers had switched elution order between chromatographic processes based on the gas chromatograms for each fraction. Figure 6 represents the last three LC fractions and illustrates that the second LC fraction is actually the second mono-chlorinated isomer (Fig. 6, fraction 2, 13.07 min) that elutes in the GC method. The complement is true for the third LC fraction (Fig. 6, fraction 3, 11.30 min).

Structural Characterization

Other analytical techniques were attempted to validate GC peak assignment to specific isomeric chemicals. Fragmentation of individual masses in an ion-trap mass spectrometer (LTQ, Thermo-Finnigan, Waltham, MA) was used to determine whether the mono-chlorinated isomers would produce different molecular fragments providing unique substituent arrangement. Owing to the stable fused ring system, the first fragment obtained involved a loss of 17 Da and MS/MS isolation, and fragmentation of the *m/z* 254 subsequently resulted in chlorine atom loss. Once the chlorine atom is removed, it renders further analysis impossible for isomeric determination. Infrared (IR) spectroscopy was also investigated to determine whether the two isomers would result in different spectra. IR spectroscopy is capable of distinguishing aryl isomers although multiple- or fused-ring structures complicate spectral interpretation (15). Unfortunately, not enough material was available for the performed analyses and assignments could not be confirmed. MS/MS and IR spectroscopy were attempted first because in-house instrumentation was available.

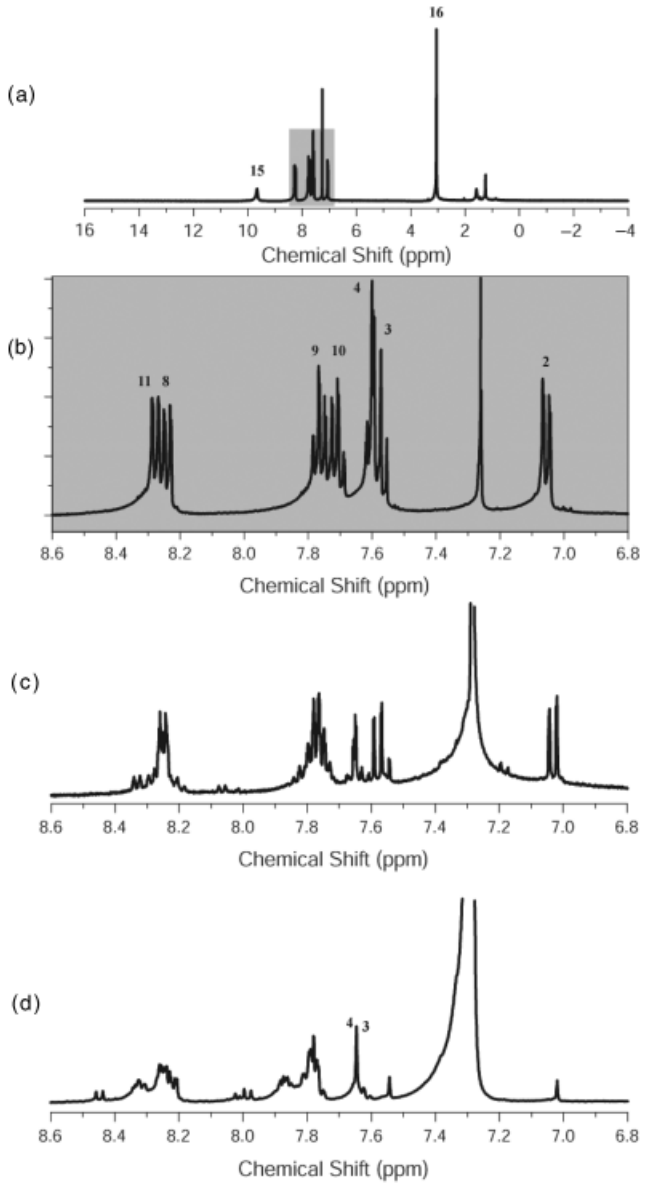


FIG. 7—*^{1}H NMR spectra for (a) 1-(methylamino)anthraquinone (MAAQ) and expanded ^{1}H NMR spectra for (b) MAAQ, (c) para-chlorinated isomer, and (d) ortho-chlorinated isomer illustrate proton resonance changes after chlorine substitution.*

^{1}H NMR spectroscopy of the parent compound, 2 mg MAAQ in 0.5 mL $CDCl_3$, is depicted in Fig. 7*a* and results in nine resonance peaks for each unequivocal proton on the molecule (see labeled positions in Fig. 1). MAAQ ^{1}H NMR resonances have previously been assigned (16). Resonances that occur between 6.5 and 8.0 ppm are important for the mono-chlorinated isomers because they will exhibit the greatest change upon chlorine substitution. Resonances in this spectral range will disappear and/or shift depending on the proton substituent that is replaced by chlorine. Figure 7*b* shows an expanded portion of the MAAQ ^{1}H spectrum (Fig. 7*a*) and contained peaks for the ortho position (2: 7.06 ppm), the meta position (3: 7.57 ppm), and the para position (4: 7.61 ppm).

The ^{1}H NMR spectrum for the second LC fraction (third GC peak) is depicted in Fig. 7*c*. Chlorine substitution occurs on the para position for this isomer because the ortho doublet at 7.03 ppm (position 2) was still present and intensity loss of resonance peaks at 7.61 ppm occurred. Therefore, the second LC fraction (8.24 min) was identified as 4-chloro-1-(methylamino)anthraquinone. There were still some resonance peaks present in the para position chemical shift region but these probably indicate the presence of decomposition products. The liquid and gas chromatograms indicate other peaks, and fraction collection probably did not prevent complete isolation of the para mono-chlorinated isomer.

The ^{1}H NMR spectrum for the third LC fraction (second GC peak) is presented in Fig. 7*d*. Chlorine substitution occurs on the ortho position because the ortho resonance at 7.06 ppm (position 2) disappeared with some complementary intensity loss for the meta resonances (position 3) due to proton coupling loss. Signal-to-noise for this compound is not as high compared with the para fraction but this is because the original reaction mixture contained twice as much para product than ortho product. The single peaks flanking the chloroform solvent proton resonance (7.28 ppm) are ^{13}C satellite peaks. One other useful spectral characteristic not depicted in the figure was the larger downfield chemical shift observed for the ortho isomer methyl group resonances (position 16) due to the chlorine atom proximity. Chemical shifts for the methyl group are 3.05, 3.09, and 3.38 ppm for MAAQ, para mono-chlorinated MAAQ, and ortho mono-chlorinated MAAQ, respectively. Therefore, the third LC fraction (10.94 min) was identified as 2-chloro-1-(methylamino)anthraquinone. Attempts at obtaining a ^{1}H NMR spectrum for the di-chlorinated product resulted in low signal intensity for the dilute compound concentration collected.

Casework Mock Scenario: Where Is the Catalyst?

The question that still remains is how this reaction occurs when a criminal bleaches bank notes that have been stained with MAAQ dye. The reaction catalyst is $FeCl_3$ and, without $FeCl_3$, the reac-

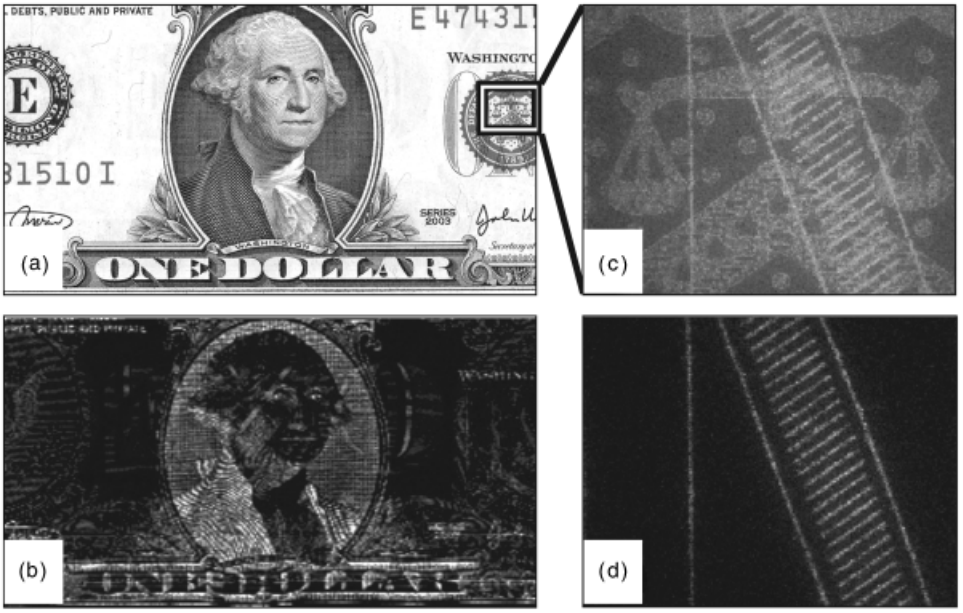


FIG. 8—*Elemental iron maps of a dollar bill indicate that iron content correlates directly with black ink location. (a) Mosaic image of a dollar bill; (b) micro X-ray fluorescence elemental map of iron (K_α); (c) Scanning Electron Microscope (SEM) backscatter electron image of a dollar bill region where black ink overlaps the green ink of the treasury seal; (d) SEM elemental map of region (c) showing that iron is associated with black, but not green ink.*

tion will not proceed at an appreciable rate. The assumption has been made that criminals are not intentionally adding the catalyst to the bleach reaction. Only one other alternative remained concerning the catalyst's source—the substrate. Federal Reserve Notes do contain iron and there are numerous scientific experiments that can be performed to illustrate this fact. Specific substrate locations of iron can be visualized by X-ray fluorescence and/or SEM-EDS; thus, experiments were performed to investigate iron (Fe) content in Federal Reserve Notes.

Elemental maps of a U.S. one-dollar bill were created using μ-XRF and SEM-EDS to determine the distribution of Fe on bank notes. Both techniques qualitatively confirmed that Fe is concentrated in the black ink and is not detectable in the paper (Figs. 8*a–d*). The black ink, shown in the mosaic dollar bill photo (Fig. 8*a*), corresponds directly to the Fe distribution mapped by the μ-XRF stage-scan (Fig. 8*b*). Note that this map shows the location of the Fe-rich black ink on both sides of the currency due to the large penetration depth of the X-ray source and the density of printing ink. A higher resolution SEM image (Fig. 8*c*) and elemental Fe map (Fig. 8*d*) of the treasury seal with black ink overlapping green ink further indicates that Fe is concentrated only in the black ink. Fe found on Federal Reserve Notes is likely the Fe source responsible as the reaction catalyst during MAAQ chlorination upon bleach addition.

Conclusion

A new, facile synthetic route was determined for chlorinated MAAQ derivatives. All compounds were produced in solution as a mixture and were separated and analyzed with complementary analytical techniques. Products were isolated and probed with NMR to unambiguously assign the chromatographic peaks to mono-chlorinated MAAQ isomers: 2-chloro-1-(methylamino)anthraquinone and 4-chloro-1-(methylamino)anthraquinone. New insights were proposed to understand the chemical reaction that occurs when a suspect attempts to remove colored MAAQ stains from banknotes with chlorine bleach.

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