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 **Research and Technology**

Analysis of a Suspect Explosive Component: Hydrogen Peroxide in Hair Coloring Developer

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Introduction

The objective of this article is to demonstrate the approach used for the analysis of a suspect explosive component submitted as case evidence. Samples of evidence taken from the home of a suspect who was under suspicion for producing bombs were submitted to the FBI Laboratory. The evidence included two five-ounce cans labeled citric acid, five tubes labeled hexamine, an empty one-pint bottle labeled Welloxide® liquid stabilizer developer, and a small vial containing a portion of the liquid originally in the Welloxide® bottle. Welloxide® is a hair coloring developer that contains hydrogen peroxide (H₂O₂) to oxidize hair in the coloring process. The extremely unstable explosive material, hexamethylenetriperoxidodiamine (HMTD), can be produced by combining 45 g of 30% hydrogen peroxide, 14 g of hexamine, and 21 g of powdered citric acid (Urbanski 1985). To demonstrate, in this case, that all the required components to prepare HMTD were present, it was necessary to verify the contents of the containers as labeled. This article specifically concerns the analysis of the Welloxide® liquid developer to determine if there was sufficient H₂O₂ to produce HMTD. Analysis schemes to identify HMTD explosive have been reported (Reutter et al. 1983; Zitrin et al. 1983), but in this case it was necessary to identify each precursor. Because peroxides are highly corrosive, care was taken to use a method that would not damage instruments during the chemical analysis. Infrared (IR) and Raman spectrometry techniques were chosen for the analysis because both offer safe sampling methods.

Forensic IR analysis is a well-established method (Bartick and Tungol 1993; Suzuki

1993), and Raman spectroscopy is an emerging method in forensic analysis. Using an attenuated total reflectance (ATR) accessory with a horizontal internal reflection element (IRE) is a convenient IR analysis technique for liquid and solid samples (Harrick et al. 1992). Liquid samples can be deposited on the IRE for direct analysis with no sample preparation. Raman spectroscopy, however, has the advantage over IR in that samples can be analyzed directly through glass vials and in water without interference from water absorption. Raman spectral bands result from scattered energy caused by an electron dipole moment (polarization) that produces a shift from an excitation laser frequency (Colthup et al. 1990). Raman peaks are usually plotted as intensity versus wavenumber shift (cm^{-1}). IR peaks result from an absorption of energy caused by molecular dipole moment vibrations and are plotted as intensity versus frequency in wavenumbers (cm^{-1}). Raman and IR are considered complimentary methods but are frequently used independently. By using both of these methods, more chemical structural information can be obtained.

In 1928 C. V. Raman of India discovered the Raman effect, and in 1930 he was awarded the Nobel Prize for his discovery. Until recently, Raman spectroscopy has not been used widely outside of research laboratories. It was difficult to perform Raman analysis because the instrumentation was very complex, poor response was obtained, and samples fluoresced when subjected to the excitation source. When samples fluoresce, the spectral features are often washed out. Fluorescence often masked the Raman signal and yielded poor or no spectral information. Recent developments in Raman instrumentation, including dispersive and Fourier transform (FT) instruments, have reduced these problems. Advances include improved excitation lasers, holographic notch filters, monochromators, fiber-optic sampling probes, and charge-coupled-device (CCD) detectors (Chase 1994). Current Raman spectrographs have become fast and easy to use with far fewer difficulties than earlier instruments, and as a result, Raman spectrometry has gained new interest in research, industry, and forensic science for routine analysis. Particular interest has developed with forensic and law enforcement personnel because of the potential to analyze unopened containers of possibly hazardous samples both in the laboratory and with portable instruments in the field.

Experimental

IR analysis was conducted on a Model 710 Fourier transform infrared (FT-IR) spectrometer (Nicolet Instruments, Madison, Wisconsin). An ACS grade 50.0% wt./vol. H_2O_2 reference standard in water was analyzed using an ATR accessory (Spectra-Tech, Shelton, Connecticut) with a horizontally placed zinc selenide IRE. Approximately 5 ml of the standard was pipetted onto the IRE to fill the trough. To obtain IR spectra of H_2O_2 and water, 128 scans were made at 4 cm^{-1} resolution within the range of $4000\text{--}700 \text{ cm}^{-1}$. A Model 2000 Microscope System (Renishaw, Gloucestershire, United Kingdom) with a 781-nm Renishaw diode laser was used for the Raman analysis. A macro sampling device was mounted on the microscope stage, and a 5x power, right-angle objective was used to focus on the samples in glass vials. Standards of H_2O_2 were prepared starting at 50.0% and diluted within a range to 3.0% wt./vol. A continuous grating scan was used from $3000\text{--}200 \text{ cm}^{-1}$ with an exposure time of 60 seconds at 100% laser power. The instrument frequency calibration fell within range of the ASTM E1840-96 guideline using a naphthalene standard. The standards were analyzed three times each, and calibration plots were prepared based on peak height and area. Three analyses were conducted on Welloxide® liquid developer that had been placed in a glass vial in the same manner as the standards.

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Results and Discussion

The IR spectrum of the 50.0% reference standard is shown in Figure 1A. The band of greatest significance to identify H_2O_2 , the O–O stretching at 876 cm^{-1} (Bellamy 1975), is not observable in the standard spectrum. The major broad bands near 3300 and 1640 cm^{-1} are from the water O–H stretching and bending, respectively. The small broad band near 1400 cm^{-1} results from the O–H bending of the H_2O_2 , but the assignment for the band near 2820 cm^{-1} is unknown. In an attempt to remove the large water contributions, a water blank was scanned and is shown in Figure 1B. This spectrum was subtracted from the H_2O_2 spectrum in Figure 1A, and the resulting spectrum is shown in Figure 1C. The H_2O_2 indicating peak near 876 cm^{-1} , from the O–O stretching vibration is small but observable after the subtraction. A large peak is not expected in the IR because the symmetrical shape of the H_2O_2 molecule (H–O–O–H) does not have a significant molecular dipole moment. The small size of this peak makes it difficult to positively identify H_2O_2 by IR alone. To obtain a more definitive spectrum of H_2O_2 , the 50.0% H_2O_2 standard was scanned using Raman spectroscopy. Figure 2 shows the standard spectrum obtained while contained in a glass vial. The 876 cm^{-1} band in the Raman spectrum is significantly larger than the same band in the IR spectrum. The spectrum of the Welloxide® liquid developer under investigation in Figure 2 shows the peak of interest clearly visible with significantly less intensity. The recorded 876 cm^{-1} peak of the standard and developer agrees with reported Raman H_2O_2 spectra in water (Vasque et al. 1997).

Analysis of the H_2O_2 standards produced calibration curves with correlation coefficients of 0.9944 by peak height and 0.9929 by peak area measurement of the 876 cm^{-1} band. The standard deviations were 0.49% and 0.77% for height and area respectively. For three measurements, the average concentration of the liquid developer in question was 6.70% by height and 6.33% by area measurement. Figures 3 and 4 show the calibration plots for each measurement type. Figure 5 shows the liquid under investigation with a slightly less peak intensity than that of the 7.0% standard sample. To produce HMTD, a 30% H_2O_2

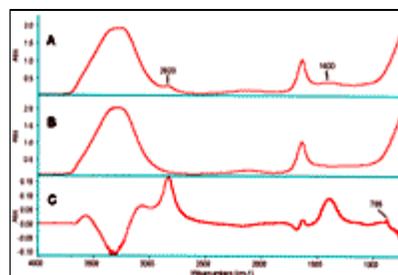


Figure 1. Infrared spectrum of a 50% H_2O_2 standard in water (A); water spectrum alone (B); and the difference spectrum of the standard minus the water spectra (C). [Click for enlarged image.](#)

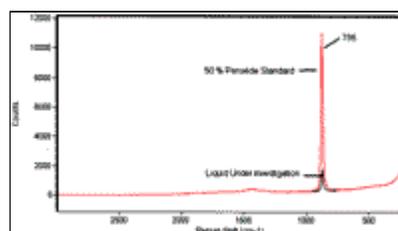


Figure 2. Raman spectra of a 50% H_2O_2 standard in water and the Welloxide® liquid stabilizer developer under investigation. [Click for enlarged image.](#)

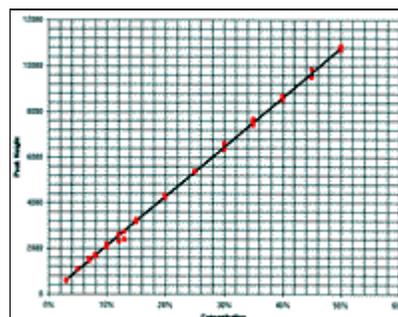


Figure 3. Calibration plot of the hydrogen peroxide standards by peak height. [Click for enlarged image.](#)

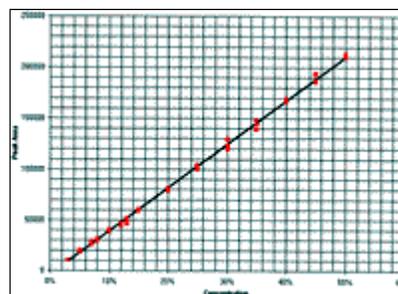


Figure 4. Calibration plot of the hydrogen peroxide standards by peak area. [Click for enlarged image.](#)

in water solution is normally used. However, the age and storage conditions of the H_2O_2 sample in this particular case were unknown, and the percentage could be reduced gradually on the basis of these variables.

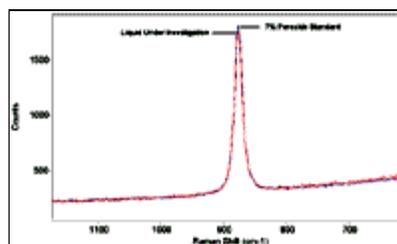


Figure 5. Raman spectra of the Welloxide® liquid stabilizer developer under investigation compared to a 7% H_2O_2 standard. [Click for enlarged image.](#)

Conclusion

The components found in the subject's possession, each with confirmed identification, could be used to produce HMTD. Raman spectroscopy shows the distinct presence of the hydrogen peroxide O–O stretching peak at 876 cm^{-1} . The IR peak is not observable until the water spectrum is subtracted, and still the peak of interest is weak. The analysis by Raman spectroscopy is carried out directly through the sample glass vial, making the analysis of this corrosive substance safe and rapid. Raman analysis is clearly the method of choice to determine the concentration of H_2O_2 , and with sufficient quantity, the Welloxide® liquid stabilizer developer can be concentrated for use in the production of HMTD.

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