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The Disposal of Unknown Waste Chemicals Using FT-Raman Spectroscopy as an Identification Tool

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KEYWORDS

FT-Raman, sample identification, chemical disposal, spectral libraries

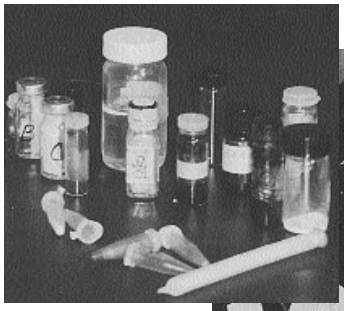
INTRODUCTION

A common problem of many laboratories today is the gradual accumulation of chemical samples; many of which are unidentified, mislabeled or changed from their original state. Over the course of decades when chemical storage rules were less stringent, large collections of unknown materials have been created. These present hazards to humans and the environment, occupying valuable space and violating safety guidelines and audit programs.

In many cases, bottles are stored without proper identification labels or Material Safety Data Sheets (MSDS). In some situations, chemical containers have been stored and forgotten about in dumpsites outside laboratories where weather has worn off the labels. Due to strict rules for disposal and the fact that many more chemicals have been identified as health hazards for human beings (or life in general), the costs for disposal are very high; thus chemists have to find quick and easy ways to identify the samples. The ideal procedure would leave the sample in the bottle to eliminate human contact with the unknown chemical.

Infrared spectroscopy is an excellent technique for the identification of unknowns. However, due to the nature of the technique, sample preparation (pressing the sample in a KBr pellet or filling a liquid transmission cell) is usually necessary. Preparation techniques may not only change the properties of the material but also expose the analyst to the sample. Near-infrared spectroscopy can be performed through glass, but the information in a NIR spectrum is secondary, i.e. the bands are not due to fundamental vibrations of the bonds. Overtones and combination bands are measured making interpretation difficult and in many cases impossible. Furthermore, no large spectral databases for NIR exist.

Raman spectroscopy provides information on fundamental vibrations *and* can measure directly through glass bottles or other packaging materials. However, the use of visible lasers results in fluorescence, and the Raman bands can be overwhelmed by an intense fluorescent background. Green excitation at 488 nm will only provide a useful Raman spectrum for about 20% of real life samples. Using "far-red" lasers (e.g. 785 nm) increases the chance of getting a Raman spectrum, but it appears that many glass bottles show a strong fluorescence spectrum at this excitation energy, peaking in the region around 1,500 cm^{-1} of the shifted spectrum. The use of near-infrared lasers eliminates most problems related to fluorescence since the chance that a fluorescence level is excited is dramatically decreased.[1] Commercially available FT-Raman spectrometers take advantage of the low energy of a near-infrared laser and provide high sensitivity and extreme ease of use. Since we are concerned with the identification of a broad range of materials, the large FT-Raman databases available are necessary tools. Aldrich Chemical Co. (Milwaukee, WI) in cooperation with Nicolet, has released a commercial FT-Raman database of over 14,000 compounds. The existence of these libraries makes the FT-Raman technique ideal for the quick identification of many unknowns in glass bottles which is necessary prior to their disposal.



EXPERIMENTAL AND RESULTS

In many application laboratories, a large variety of samples have accumulated over the years. In order to comply with ISO 9000 guidelines and other GLP procedures, old materials must be collected and disposed. Unidentified materials will not be accepted for disposal. Before it was standard practice to send chemicals with MSDS documentation, many samples were received without proper labeling, and in other cases no labeling, for proprietary reasons. Disposal of samples without identification can add several hundred dollars per sample to cover identity-testing costs. FT-Raman spectroscopy was the technique of choice to quickly identify a very large set of unknowns. Over 150 samples were identified without any human exposure, many of which were discovered to be highly toxic. It was estimated that the cost of outside identification of roughly twice this number of samples would pay for a dedicated FT-Raman instrument.

Sample bottles are placed directly into the FT-Raman 960. The excitation laser is focused on the sample through the glass, making it possible to analyze dangerous unknowns without removing them from their containers.

EXAMPLES

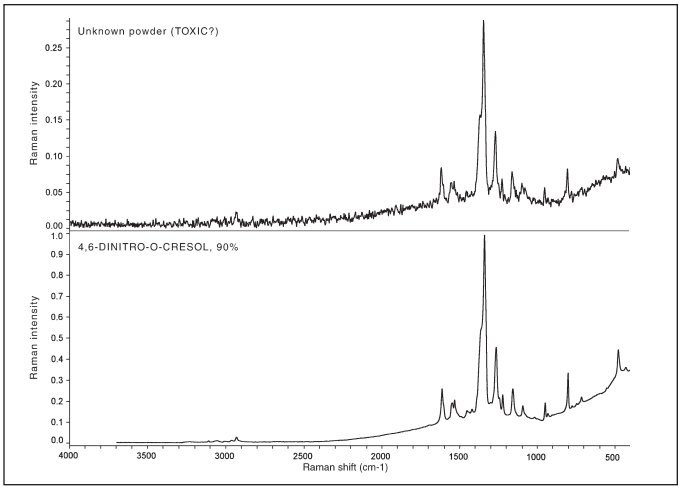


Figure 1: Small amount of unidentified powder…the only label on the amber bottle was a skull and crossbones. Sample spectrum through bottle (256 scans, 4 cm^{-1} resolution, Ge detector) and first library match; 4,6 – Dinitro-o-cresol.

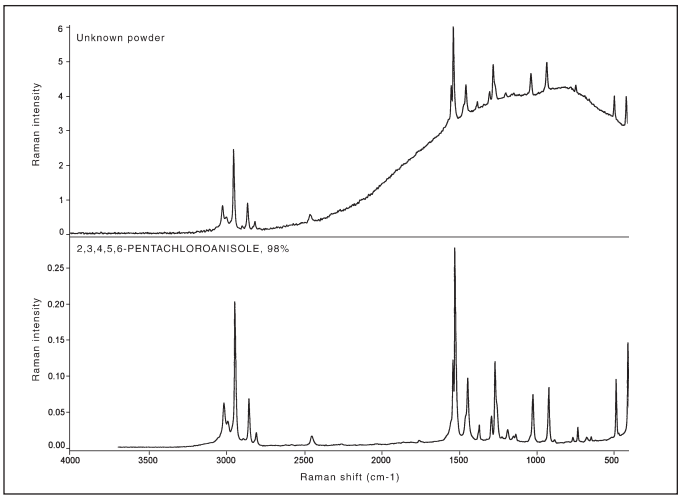


Figure 2: An unknown sample exhibiting a sloping baseline due to fluorescence[1], shown with the first library match. With the near-infrared laser, the Raman spectrum is strong enough to be seen easily over the fluorescent background. 2,3,4,5,6 – Pentachloroanisole, 4 cm^{-1}, 64 scans, Ge Detector, 450 mW laser power.

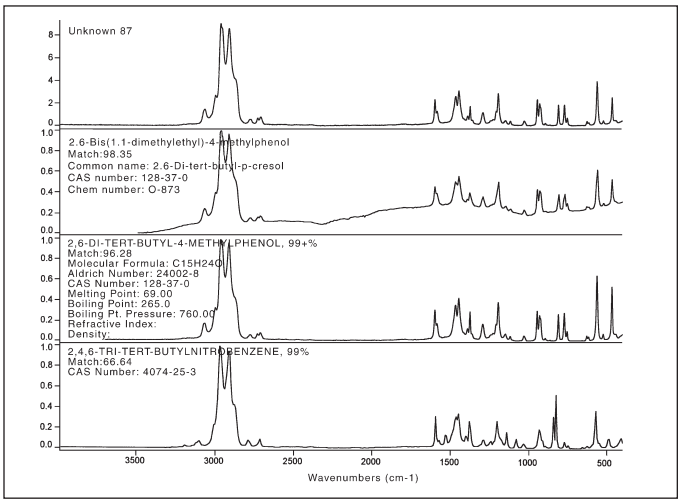
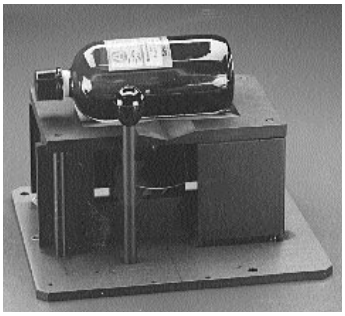


Figure 3: Unknown liquid identified as 2,6-Di-Tert-Butyl-4-Methylphenol by its Raman spectrum, shown with first three library matches. Sample was run in the bottle at 4 cm^{-1} resolution, 64 scans, using a Ge detector and a laser power of 450 mW.

For the experiment, a dedicated Nicolet FT-Raman 960 instrument, using both an InGaAs detector and a liquid nitrogen cooled Ge detector for the more challenging samples, was used. Instrumental conditions were set depending on the nature of the sample, using laser powers at the sample of between 2 and 500 mW and between 4 and 1,000 scans at 4 cm^{-1} resolution were co-added. Using this method, FT-Raman spectra of more than 80% of the unknown samples were acquired. More than 70% of the unknown samples were identified by library searching and spectral interpretation techniques.



The FT-Raman bottle holder was designed for quick analysis of powders and liquids without removing them from their containers.

CONCLUSION

FT-Raman spectroscopy is an ideal technique for rapid identification of unknown chemicals. A Nicolet Raman 960 spectrometer was used in conjunction with FT-Raman spectral libraries to identify many unknown chemicals for disposal, saving thousands of dollars in identity-testing fees. The accumulation of hazardous materials was eliminated safely, very quickly and without human exposure.

FOOTNOTES

1. Sloping baselines due to fluorescence are frequently encountered, even when a NIR laser is used. This is mainly due to the nature of the samples: contaminations and decomposition products often show fluorescent properties. However, the Raman spectrum is in most cases superimposed on the background upon 1,064 nm excitation. When visible lasers are used, even the far-red 785 nm laser, the Raman spectrum is completely swamped due to Shot Noise associated with the fluorescence radiation.

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