



WHITE PAPER

On-site detection of hexavalent chromium in protective paint primers

Easily identify target compounds in the presence of fluorescent interferences with handheld Raman.

Zinc chromate pigment was once widely used in the aeronautics industry due to its anti-rust and anti-corrosive properties. As an additive in paint primer coatings for steel and aluminum surfaces, it demonstrated superior performance in preserving the structural integrity of military vehicles, as well as commercial and personal aircraft. However, long-standing concern over health hazards related to zinc chromate exposure led to stringent regulation in the 1970s and then to the gradual withdrawal of zinc chromate-containing products in commercial

and industrial applications. This creates a need for robust, on-site forensic technologies for rapid and accurate identification of zinc chromate and other hexavalent chromium compounds in complex test samples. Handheld Raman is a well-known solution that meets the criteria for fast and flexible identification of materials, but the target signal from 785 nm systems can be confounded by fluorescence, a particular problem with mixtures, paints, and dyes. In this White Paper, the handheld MIRA XTR DS analyzer is shown to exceed performance expectations for 785 nm Raman for the analysis of potentially chromium-containing paints.

Zinc Chromate

Surface passivation of aluminum alloys using zinc chromate-based paint primer has been a standard practice in aircraft manufacturing for nearly a century. In addition to providing a superior anti-corrosive protective barrier for surfaces exposed to the elements, chromate coatings demonstrate the ability to self-heal after adverse chemical and physical interactions with the environment [1]. Other commercial applications include widespread use as an anti-rust additive in spray paints for metal surfaces, anti-fouling primer for the underside of maritime vessels, and pigment in artists' oil paints. However, zinc chromate paints are very sensitive to photolytic degradation and therefore their use by artists has declined over time [2].

Despite their excellent anti-corrosion properties, extensive evidence suggests that chronic exposure to hexavalent chromium ions (Cr^{6+}), such as in zinc chromate, can result in cytotoxicism and cancer [3–5]. This has led to the regulation and restriction of products that contain hexavalent chromium in manufacturing and finishing facilities, with the end-goal of fully transitioning to suitable alternatives [6]. In the United States, the Occupational Safety and Health Administration (OSHA) classifies zinc chromate as a hazardous substance, and has gone so far as issuing several health citations to Northrup Grumman in 2015 for failure to minimize worker exposure to chromium in a painting facility [7]. European Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulations are even more stringent, stipulating step-wise bans on different hexavalent chromium species over the next five years [8].



FLUORESCENCE AND 785 NM RAMAN SPECTROSCOPY

It is undeniable that interference from fluorescence presents the greatest challenge to expanding detection capabilities for 785 nm Raman spectroscopy. Fluorescence may arise from laser excitation of the material itself or from other substances that are present in sample mixtures. This overwhelms the Raman signal, obscuring signature peaks required for selective and sensitive analyte detection (**Figure 1**).

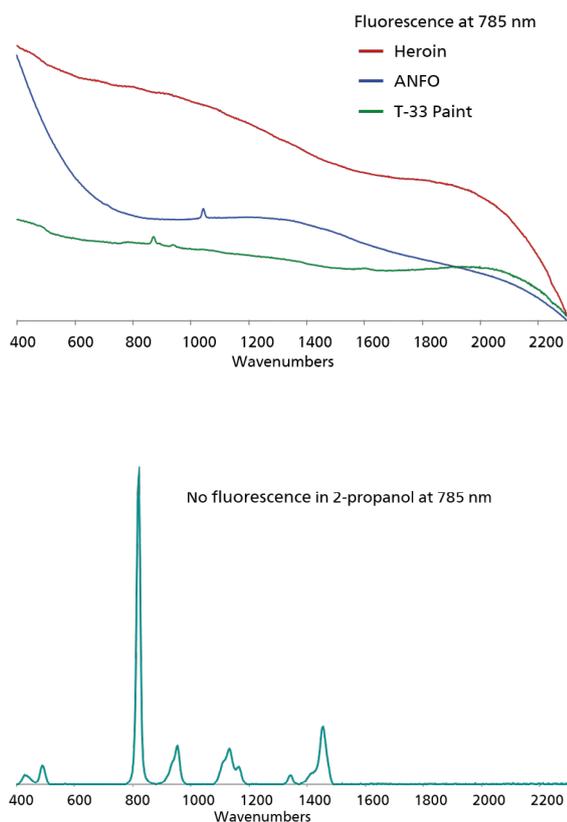


Figure 1. Compounds that exhibit fluorescence with 785 nm Raman excitation, top. On the bottom is a typical Raman spectrum of a chemical that does not fluoresce under laser excitation.

This obstacle can be addressed using 1064 nm laser excitation, as most substances do not absorb light at this wavelength and, therefore, do not fluoresce. Long wavelength excitation is a poor solution, as this requires higher laser powers and longer acquisition times to compensate for reduced Raman scattering. As a result, samples are prone to laser damage *and* instrument battery lifetimes are significantly shortened. Handheld 1064 nm Raman systems use short-wave infrared detectors that require cooling and large batteries, which results in a substantial increase in cost, size, and weight.

FLUORESCENCE-FREE DETECTION OF CHEMICAL COMPOUNDS WITH XTR

Metrohm Raman's solution for the acquisition of fluorescence-free spectra is MIRA XTR DS, which incorporates the design and functionality of the handheld 785 nm MIRA DS with a new capability that selectively eXTRACTs the Raman signal from fluorescence emissions. Fluorescence rejection at 785 nm provides higher sensitivity and resolution, as well as a much wider scope of applications amenable to Raman spectroscopy. MIRA XTR DS provides users with a comprehensive and versatile material identification test solution for field operations.

BENEFITS OF THE DEVICE INCLUDE:

- Seamless smart operation from login to results
- Very broad chemical identification capabilities due to our large libraries
- Informed decision-making and actionable intelligence through interface with HazmasterG3®
- Flexible, on-site sampling with our suite of interchangeable Smart Tip sampling attachments
- Accurate identification of target substances, even in heterogeneous mixtures, with Orbital Raster Scan
- All in a compact, rugged form factor that fits in your pocket.



Figure 2. MIRA XTR DS supports accurate, simple on-site materials testing with its compact size and extensive libraries.

Methodologies

DISCERNING THE CHROMATE PEAK

In the Raman spectrum, each discrete peak corresponds to a stretching or bending vibration associated with a specific functional group in its molecular environment. In order to establish a pattern for the chromate peak in hexavalent chromium compounds, a range of compounds were purchased from Sigma Aldrich, placed in disposable glass vials, and sampled through the glass with MIRA XTR DS and the Long Working Distance (LWD) point-and-shoot Smart Tip. This method for sampling of chromates and other potentially harmful materials is particularly attractive, as it permits fast and accurate data collection with no sample contact.

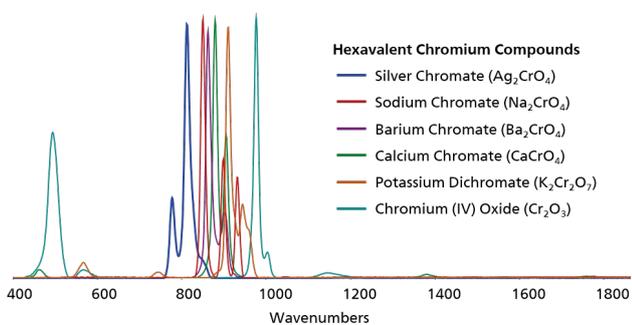


Figure 3. MIRA XTR DS Raman spectra of hexavalent chromium compounds

Overlaid MIRA DS XTR-processed 785 nm Raman spectra collected for six hexavalent chromium compounds

each contain intense, highly-resolved signal peaks in the 800–1000 cm⁻¹ region of the spectrum (Figure 3). Studies of numerous chemicals containing chromium have rigorously shown that features in this region of the Raman correspond to Cr–O stretching modes [9, 10]. It must be noted that the flat baselines and high resolution peaks evident in these raw spectra are typical of XTR® results.

AUTHENTICATING «CHROMATE» PAINTS

Having demonstrated a strong Raman response for pure chromium compounds, the performance of MIRA XTR DS was evaluated using several commercial paints. The goal of this was simple confirmation of the chromate peak using XTR routines, with the added expectations that the same samples tested with 785 nm would result in unresolved spectral fluorescence, while 1064 nm testing might burn or otherwise decompose the paint samples. The tested paint samples included MarPro Zinc Chromate Primer, which is labelled as a paint primer for protecting the underside of aluminum boats. Three model kit paints were also included: Testors Matte Zinc Yellow, and Mission Models and Model Masters Green Zinc Chromate. Finally, an authentic strontium chromate paint standard was included for comparison with the commercial paints.

MIRA XTR DS was used to collect 785 nm data. A handheld 1064 nm Raman system was also used for analysis. Paint samples purchased from vendors were placed in disposable glass vials and tested through the glass



with LWD and also on exposed surfaces after drying using the Short Working Distance (SWD) attachment. Regardless of the sampling method, Smart Acquire on MIRA XTR DS automatically optimized acquisition parameters such as laser power, integration time, and multi-spectrum averaging for the highest quality result.

As seen in **Figure 4**, XTR provided well-resolved spectra for all paint samples. Interestingly, the data is sufficient to indicate that none of these paints display peaks in the Cr–O stretching region, aside from the known strontium chromate sample. Thus, the authenticity of these other commercial products must be questioned. Efforts to obtain quality spectra for all paint samples using 785 nm and 1064 nm interrogation were unsuccessful.

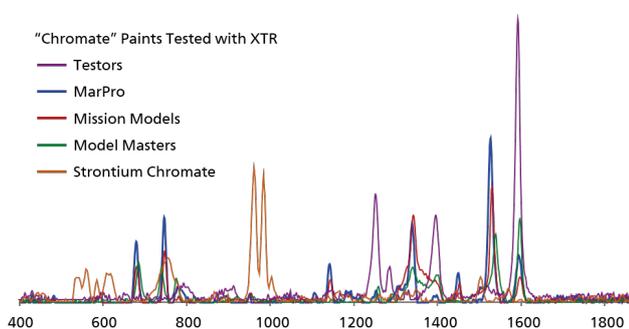


Figure 4. Paints labelled as «chromates», tested with MIRA XTR DS, exhibited no spectral peaks in the Cr–O stretching region.

Without XTR, 785 nm laser excitation yielded spectra that were overwhelmed by fluorescence. The 1064 nm

system yielded low-resolution spectra and damaged all test samples, despite the use of a dedicated 1064 nm sampling attachment that was designed to enlarge the area of interrogation by spreading out the laser light, with the intention of preventing damage to the sample. Due to the increased absorbance of light by colored substances, pigmented paints will tend to burn or ignite when interrogated with a high power laser. Not only does MIRA XTR DS use a lower power 785 nm laser, but all MIRA systems are equipped with Metrohm Raman’s proprietary Orbital Raster Scan (ORS™) technology. ORS quickly moves the laser over a large area, collecting more representative data and preventing sample degradation.

REAL WORLD RAMAN

As an additional demonstration of the power of MIRA XTR DS for detecting chemical compounds in challenging matrices, the paint used inside the landing gears of a Lockheed T-33 military jet airplane was sampled. According to all reports, zinc chromate primer was used extensively in US military vehicles. Uniquely, interior aspects were often primed but left unpainted, making this a legitimate test case for the presence of hexavalent chromate. Testing was conducted at a National Guard museum in Cheyenne, Wyoming USA. Using MIRA XTR DS with intelligent Universal Attachment (iUA) Smart Tip, the exposed outer surfaces of the landing gear on a retired Lockheed T-33 training jet were queried.



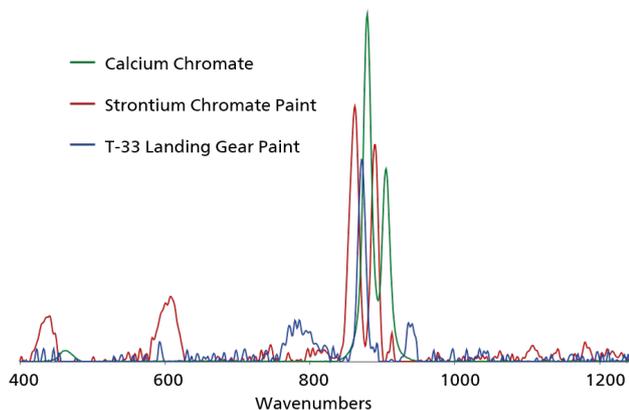


Figure 5. An unknown paint suspected of containing chromate agrees with Raman spectral chromate peaks found in known samples.

The spectrum for T-33 landing gear paint is shown in blue in **Figure 5**, accompanied by the pure calcium chromate spectrum used herein to confirm peak agreement among chromium compounds (green) and the strontium chromate paint spectrum referenced in **Figure 4** (red). Each of these spectra is characterized by prominent peaks in the Cr–O stretching region of the spectrum. The T-33 peak at 872 cm^{-1} is in excellent

agreement with forensic Raman analysis of zinc potassium chromate pigment (i.e. zinc yellow) in oil paintings [11–13]. As a zinc chromate standard is currently unavailable for testing, reliance on peer-reviewed literature and logic is necessary in order to conclude that the primer used in the T-33 aircraft was likely zinc chromate. **The most remarkable aspect of this real-life test case is the demonstrated capability of positively identifying zinc chromate in a complex matrix like aged paint primer.**

CONCLUSION

MIRA XTR DS provides users with the most advanced, versatile, and compact handheld Raman system currently available on the market. The ability to extract highly-resolved spectra from bright colored, heterogeneous, and complex matrices expands the traditional limits and suitable applications of 785 nm Raman spectroscopy. Fluorescence rejection means that handheld Raman is now positioned to rapidly and accurately conduct a broader range of forensic analyses in the field.





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