

Raman microscopic detection of chromium compounds

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Abstract. The paper is focused on performing Raman microscopy for the detection of trivalent and hexavalent chromium compounds. Raman spectroscopy has become a powerful method for material identification with the ability to differentiate the structure of the studied materials. It is important in the interests of human health and environmental protection to develop and use methods capable to measure not only the content of total chromium and but the content of toxic hexavalent chromium. Some of such methods are listed in the paper. Samples such as leather, leather processed to hydrolysate or leather waste material as well as the commonly used (yellow) paints, were used for the measurement. Evaluation was carried out on the basis of characteristic spectral features. Acquired Raman spectra show these features and can serve for qualitative analyses.

1 Introduction

Chromium finds wide industrial and commercial utilization already for decades. Suspected adverse health effects of prolonged exposure to chromium in particular on respiratory tract and skin has been known for a long time. The toxicity was clearly attributed to hexavalent form only in recent years. Problematic of hexavalent chromium belongs to widely discussed issues. It is related to human health and the environmental impact. All things considered, both are inseparately connected.

Chromium exist predominantly in two forms as beneficial trivalent and mutagenic and toxic hexavalent chromium. Therefore measurements related to potential hazard is complicated by duality of these two forms. This fact brings also stricter demands on the analytical methods to be able to differentiate compounds of trivalent and hexavalent in the samples as water, air, soil or stuff of an everyday life that are in direct contact with human organisms. One of the examples is leather goods. Approximately 80% of the world production of leather is tanned using salts of trivalent chromium, which can oxidize under various conditions to toxic hexavalent form and cause health problems [1]. Another example is painted subjects. The colour scheme of some pigments is affected by both valences of chrome. Most of the matter subjects to ambient influences and thus changes. Neither for decades admired Sunflowers by Van Gogh, do not remain the same. Old Masters before the end of the 18th century used mineral pigments for shiny yellow colour, containing toxic elements such as chromium, lead or cadmium [2]. These pigments subject to reduction of hexavalent chromium in time and are changing the shiny yellow to green.

In this paper the attention is aimed on modern spectroscopic method Raman microscopy and its potential in a field of chemical component identification. On the set of samples with various share of trivalent and hexavalent chromium the advantages and contribution of the method is demonstrated.

2 Theory

2.1 Chromium

Chromium is one of the elements with a relatively high natural occurrence on Earth and in space. Chromium compounds appear in the environment also due to human activity as an adverse side product of industrial processes. This metallic element can exist in several oxidation states, however, the prevalent forms are two - trivalent chromium (CrIII) and hexavalent chromium (CrVI). Two forms with different properties and divergent impact on human health and environment.

2.1.1 Trivalent chromium

Trivalent chromium is a biogenic element and an essential part of human daily diet. Trace amounts help to control blood sugar (glucose) and stabilize blood fat levels. CrIII deficiency can cause fatigue, stress and decrease the body's ability to remove glucose from the blood. Compounds of trivalent chromium are benign due to low membrane permeability [3].

In the environment compounds of trivalent chromium are strongly bound to the soil particles and only small amounts penetrate from a soil to a groundwater.

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Compounds of CrIII find applications for example in iron-chrome production, leather processing, manufacture of dyes and pigments, production of candles, cement.

2.1.2 Hexavalent chromium

In comparison to benign CrIII compounds, the CrVI compounds have mutagenic effects and are classified as carcinogens [4]. Compounds of hexavalent chromium cause allergic reactions, skin irritation and cancerous growth in nasal cavity, lung or in digestive tract. Significantly also affect the increase of heart disease.

The problematic of hexavalent chromium is connected also with the fact that compounds of CrIII can oxidize under various conditions to form CrVI compound. The conversion is known as well as some precursors, however the precise mechanism is complex and the details have not been clearly explained in literature yet.

Fortunately, human organisms abound by the defence mechanisms and have the ability to reduce CrVI to CrIII. To what extend is an issue for further research. Several sub-processes are discussed in [5]. Some studies show more dangerous impact of the instant high dose of CrVI compared to a similar dose obtained cumulatively in the longer term [6]. Other studies suggest, based on experimental and epidemiological data, on the incidence thresholds of CrVI in connection with carcinogenesis [7]. However, also the low-dose long-term contact with toxic elements should not be neglected.

Hexavalent chromium is a toxic element and is one of the heavy pollutants in the environment. CrVI compounds pollute air, watercourses usually as wastewaters from mainly metallurgical, leather and textile industries and penetrate into the soil from poorly secured landfills.

Compounds of CrVI find applications in metallurgical industry, chroming, welding of stainless steel, manufacture of dyes and pigments, production of chromium, printers, etc.

2.2 Methods for chromium detection

In the present time many methods allow measuring content of chromium. Often the content of chromium means total chromium (CrIII + CrVI). However, obtained results might be due to different classification of these two forms misleading in terms of safety, respectively hazard. More accurate evaluation arises from distinction of the benign and carcinogenic form, what is not always a rule when informing about chromium substances content. Separation techniques coupled with highly sensitive detection methods are needful for the analysis of the single chromium forms. For the detection of CrVI are recently used methods as [8]:

- Ultraviolet-visible spectrophotometry (UV-VIS) enables experimental identification of concentrations of hexavalent chromium in ppb in water and solutions. It is used as standard method. Detection limit of this method is about 50 µg/l.

- Inductively coupled plasma mass spectrometry (ICP-MS) is capable of detecting metals and several non-metals and to perform speciation of CrIII and CrVI in concentration in order 0,1g/µl.

- Inductively coupled plasma optical emission spectrometry (ICP-OAS) is analytical flame technique for detection of trace metals. For chromium the detection limit is similar as for ICP-MS.

- Atomic absorption spectroscopy (AAS), spectrometric analytical method used to determine the content of both, trace and major concentrations of individual elements in the analyzed solution.

- X-Ray fluorescence spectroscopy (XRF), atoms of energized sample give off specific X-rays characteristic of the element. The detection limit is several orders of magnitudes worse compared with ICP-MS.

Raman spectroscopy has the potential to recognize different chemical structures on the basis of molecular vibrations [9]. Raman spectroscopy/microscopy is the method discussed in this paper for the two chromium valences detection.

Problematic is often the detection limit of the methods together with allowed limits of the CrVI in different substances and environments, and also the availability of the measuring device for a specific application.

2.2.1 Raman microscopy

Raman microscopy incorporates the advantages of Raman spectroscopy and optical microscopy. Raman spectroscopy as a vibrational spectroscopic method reflects chemical composition and structure of materials. This feature makes the method proper for material identification. Together with the advantages of optical microscopy, Raman microscopy becomes popular and finds a valuable place in laboratories worldwide in recent years [9].

Raman spectroscopy provides very specific chemical „fingerprint“ of every single chemical substance in the form of the Raman spectrum. The method is based on Raman scattering - an inelastic scattering resulting from an interaction of a photon and a molecule. In inelastic scattering photons have slightly changed wavelengths that are characteristic for specific bonds in surveyed material. Since most photons are on molecules scattered elastically (Rayleigh scattering without changing the wavelength), it is necessary to filter out of the spectrum of the strongly present wavelength of laser.

Although the fundamental phenomenon is known since thirties of the 20th century, its effective use in Raman spectroscopy occurs in about last two decades. The rebirth of this method goes hand in hand with advances in a laser, detectors and computer technology. Raman spectroscopy brings many advantages as the method is relatively rapid, non-destructive, contactless, usable for measuring through transparent glass or polymeric covering layers or containers, applicable to all states of matter and different forms, without special requirements for sample preparation.

The greatest drawback of the method is the fact that Raman scattering is a weak effect. Luminescence as

much stronger quantum effect with higher intensity can overlap Raman spectra and mask spectral information. Another disadvantage is eventual degradation of a sensitive sample when using intense laser beam.

Raman spectroscopy finds many applications in many scientific areas such as chemistry, biochemistry, material science, mineralogy, arts, medicine, also is used for pharmaceutical, forensic and security purposes.

In the last years an effort is made to produce various portable Raman spectrometers. Possibility of *in situ* and field analyses can be a significant advantage compared to laboratory techniques.

3 Experimental part

3.1. Samples and chemicals

Several types of samples containing chromium compounds were chosen for analyses by Raman microscopy. Samples are divided into two groups according to type or area of occurrence and also content of chromium.

3.1.1 Paints

Chromium exhibits many colours: yellow, orange, green, blue, violet, red, black and gray, depending on the compound. They are often present in pigments and dyes, which are used in different types of paints, colours and coatings. The attention was given to yellow paints in form of oil paint (BaCrO_4), enamel paint, painted board (by unknown colour) and powder pigment (PbCrO_4).

3.1.2 Leather

Salts of trivalent chromium are commonly used in leather industry for tanning hides. Due to oxidation and other effects traces of CrVI are also present in leather. The second group of samples with rather low concentrations of chromium is represented by the following forms: leather (pigskin); leather sample soaked in 0,1 % K_2CrO_7 solution; leather shavings (waste material of leather industry); dry matter of enzymatic hydrolyzate (resulting from the hydrolytic waste treatment) and ashes – incinerated leather sample.

3.2 Instrumentation

InVia Basis Raman microscope (Renishaw) was used to measure Raman spectra of all samples. The Raman microscope uses two lasers as light sources: argon ion laser with the maximum power 20 mW and 785 nm NIR diode laser with maximum output power 300mW. Both were tested, however, more accurate and by luminescence less affected results were those, obtained using diode NIR laser. A Leica DM 2500 confocal microscope with the resolution $2\mu\text{m}$ and 5x, 20x and 50x objectives was coupled to the Raman spectrometer.

4 Results

All spectroscopic measurements were performed directly on the surface of the sample with no special treatment. Firstly, scanning was done in common range 100 cm^{-1} - 3200 cm^{-1} with 2 cm^{-1} spectral resolution. After determination of the principle vibrational response the spectral range was reduced to the area of interest i.e. 200 cm^{-1} - 1200 cm^{-1} .

4.1 Spectral data of paints

Raman spectra of paint samples were acquired and are shown in Figure 1. Spectra reveals two pairs of similarities. Powder pigment containing PbCrO_4 and painted board exhibit a clear conformity in comparison to oil paint and enamel paint. However, oil and enamel paints shows similar spectral pattern, too. Pigment in oil

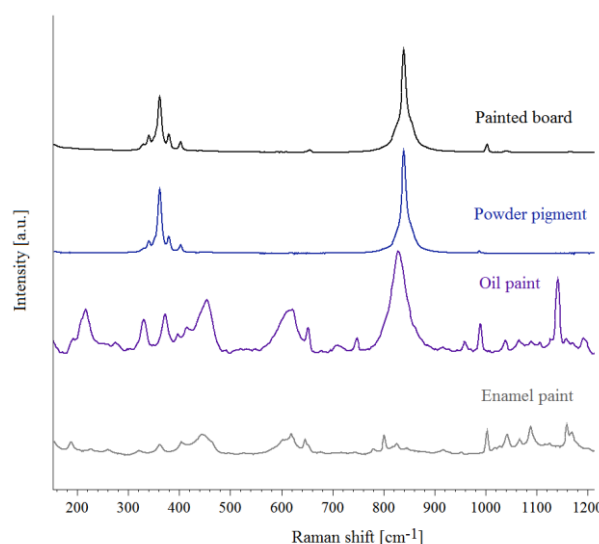


Figure 1. Raman spectra of three different yellow paints and powder pigment.

Table 1. Assignments of Raman bands of PbCrO_4 [2]

Raman shift [cm ⁻¹]	Characteristic vibrance	
135	Cr-O lattice modes	
323	Cr-O bending area	
338		orthorhombic crystalline phase
358		monoclinic phase
377		
400		
839	CrO_4^{2-} symmetric stretching	
855	CrO_4^{2-} antisymmetric stretching	
987	SO_4^{2-} symmetric stretching	

paint is known as lemon yellow, chemical composition is BaCrO_4 . With respect to the distribution of peaks in the spectra, the same pigment base can be estimated for the enamel paint.

Peak positions of both pigments are confirmed by online spectral databases Raman Spectroscopic UCL Library and Database RRUFF. Assignments of Raman bands contained in PbCrO_4 are listed in Table 1.

4.2 Spectral data of leather samples

Raman spectroscopy has the potential to distinguish CrIII and CrVI valences [10]. The crucial peaks are about 550 cm^{-1} (symmetric stretching of Cr-O-Cr) for trivalent chromium and about 900 cm^{-1} (CrO_3 vibration) for hexavalent chromium. These peaks are demonstrated in Figure 2. In Figure 3, spectral response from leather

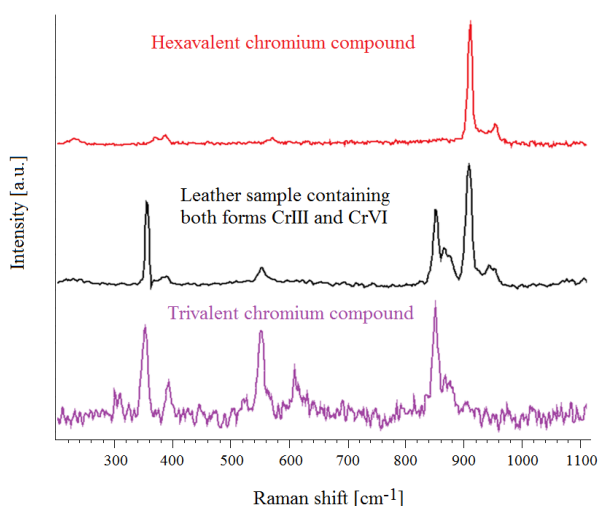


Figure 2. Raman spectra of leather containing trivalent and hexavalent chromium compounds.

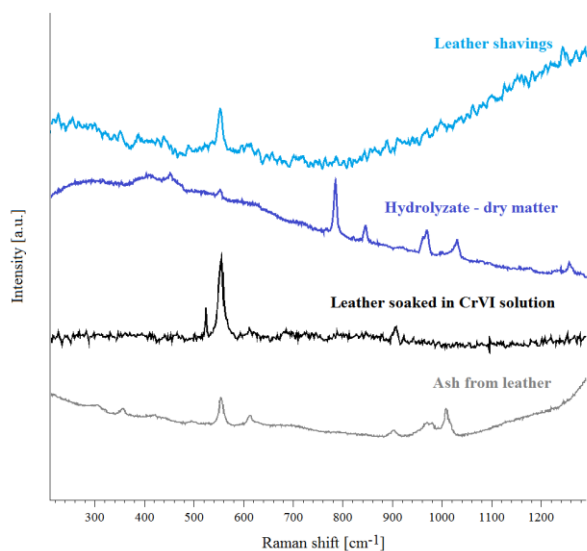


Figure 3. Raman spectra of leather shavings, collagenous protein hydrolyzate – dry matter, lather soaked in K_2CrO_7 solution, ash from leather.

shavings, dry matter of hydrolyzate, lather soaked in 0,1 % K_2CrO_7 solution and ash from the leather is depicted.

Intensities of the spectra are not normalized. However, presence of CrIII in shavings is supposed after tanning as well as in soaked leather and ash. Low concentration of CrIII in enzymatic hydrolyzate agrees to the procedure of leather waste treatment [10]. On the other hand CrVI is in higher amounts present in soaked leather due to the K_2CrO_7 solution and in the ash due to oxidation during incineration.

5 Conclusion

Possibility to detect compounds of trivalent and hexavalent chromium was demonstrated on samples of paints and pigments and leather samples in different forms by Raman microscopy. Because of significantly different characteristics of these two oxidation states of chromium it is necessary to be able to distinguish benign and carcinogenic form and measure rather hexavalent chromium than total chromium. Raman spectroscopic evaluation brings advantages mainly in terms of simplicity, rapidity, no use of chemical reagents and no special requirements for the form of measured samples.

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