

Determination of trivalent and hexavalent chromium by Raman spectroscopy

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Chromium (Cr) is a metallic element commonly occurring in nature. It can be found in rocks, volcanic dust, gases, sea water, but also as a part of living organisms including human bodies. In the environment chromium occurs in several different forms. The most prevalent oxidation states are trivalent (CrIII) and hexavalent (CrVI). CrIII is largely beneficial and as a biogenic element a necessary part of daily human diet. On the contrary CrVI is toxic, is considered a carcinogen and can negatively affect human health. CrVI occurs naturally in the environment from the erosion of natural chromium deposits, but also as a product of industrial processes.

The problem of the presence of CrVI in Cr containing products i.e. leather goods is a subject of intensive research worldwide. Also is dealt in our institute. Dechromation process of chrome-tanned waste was already resolved in our institute and the technology for this process was realized in laboratory conditions (Dolinay et al. 2008).

The real danger of Cr containing materials which are primarily in direct contact with the human body is the possibility of spontaneous oxidation of CrIII to CrVI. From the thermodynamical point of view the spontaneous oxidation is possible within a wide range of pH. The conditions of this transformation are complex and have not been explored in detail so far. Even low concentrations of CrVI compounds are hazardous for human health. When CrVI reacts with biological reductants free radicals participating in production of reactive oxygen species are generated. Excessive production of reactive oxygen species may cause DNA and proteins damage. These mutagenic characters can lead to cancerous growths in respiratory tract, kidney and urinary tract.

CrIII and CrVI compounds are produced in large quantities and people come into contact with them every day. Especially with shoes made from chrome-tanned leather. Recent upward trend in the incidence of urinary tract neoplasms not only in Czech Republic requires serious interest. There may possibly be a correlation between increasing mentioned cancer disease and rising import of relatively cheap and disputable quality (without carefully monitored content of Cr) shoes (Kolomaznik et al. 2008). CrVI can penetrate through the skin into the organism, amplified by the presence of sweat, when wearing shoes on bare feet. This is one of the threats connected with hexavalent chromium.

Products containing Cr represent another problem after loss of their utility value when they become a Cr containing waste. These waste leather products (about 240 tons of chromium for Czech Republic) are at present mostly taken to waste dumps, or combusted. Both being not an ideal solution, both accompanied by oxidation from CrIII to CrVI compounds, which endanger environment – the air, by leaching into a soil and exposure to sources of ground water. Large problems with ground water and water sources contaminated by hazardous hexavalent chromium had appeared in USA or China in the past (Ball and Izbicki 2004; Beaumon et al. 2008).

There exist several methods for chromium content in different materials evaluation. The most widely used is UV-spectrophotometric method using 1,5 diphenylcarbazide. Among other methods can be named e.g. inductively coupled plasma mass spectrometry together with liquid chromatography for water analyses, ultrasonic extraction for workplace and environmental air testing. Although knowledge of CrIII to CrVI conversion is well described in literature, the precise mechanism of the conversion is complex and details are not yet clearly explained

(Chaudhuri and Chakraborti 2003). Opponents of UV-spectrophotometric method claim that the conversion can happen during the processing.

These are the reasons for developing methods for detection the safe and the dangerous forms of Cr. A solution can offer Raman spectroscopy (RS), non-destructive, non-contact, rapid method providing specific chemical fingerprint of the samples of all states of matter.

Firstly a several readily available compounds of CrIII and CrVI as CrO_3 , Cr_2O_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ etc. were measured by RS. Other compounds and minerals containing these agents were looked in literature and available sources. Different types of samples (mainly used leather goods aiming to landfill) were tested for the presence of CrIII and CrVI. A part of the samples was directly dipped into solutions of different concentrations (0,01–5 %) of tri- and hexavalent chromium and then leached in distilled water. Both leather samples and the extracts were analyzed by Raman spectroscopy. There appeared problems with luminescence of the leather samples. They were eliminated using NIR laser (785nm) instead of Ar^+ laser (514 nm). The important result is that Raman spectra of CrIII and CrVI compounds show diversity as is displayed in Fig. 1. CrVI compounds have most intensive characteristic peak in area around 900 cm^{-1} , CrIII around 600 cm^{-1} . All the spectra were acquired using a Renishaw InVia Basis Raman microscope.

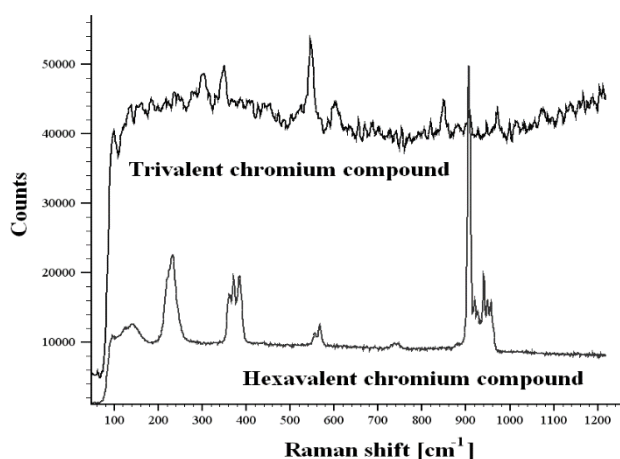


Fig. 2. Raman spectra of CrIII and CrVI compounds contained in leather samples.

Although only minor attention has been paid to this problem so far, there is increasing evidence that in the near future this problem should be taken into account. With respect to the environmental and health hazard of the waste, Raman spectroscopy seems to have potential to be able to directly qualitatively recognize the presence of carcinogenic hexavalent chromium.

Acknowledgments: This work is supported by the Ministry of Education, Youth and Sports of the Czech Republic, by the European Regional Development Fund, project CEBIA-Tech No. CZ.1.05/2.1.00/03.0089, and by the Internal Grant Agency of Tomas Bata University in Zlín, project No. IGA/FAI/2013/010.

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