

Chromium VI Issue in Leather Waste – A Technology for the Processing of Used Leather Goods and Potential of Raman Spectroscopy in Chromium Traces Detection

Karel Kolomaznik, Michaela Barinova, and Hana Vaskova

Abstract— In this paper, the authors deal with the problem of chromium present in various products and materials, and the health and environmental risks that this chromium can represent if uncontrolled. Special emphasis is given to various chrome tanned wastes generated by the leather industry. The agent that makes this waste potentially hazardous is hexavalent chromium. Its compounds can have negative effects on human health and some chromium VI salts are considered carcinogens. The authors present the risks of spontaneous oxidation of trivalent chromium to its hexavalent form in various conditions, as well as an analytical method for detection of small concentrations of both forms of chromium using Raman spectroscopy. Raman spectra of hexavalent chromium and simultaneous detection of the two valences of chromium obtained from leather samples are presented. Another important issue addressed in this paper are technologies processing various kinds of chrome-tanned waste. From the technological point of view, there are several ways of handling primary leather waste, but no satisfactory technology has been developed so far for the secondary waste (manipulation waste, e.g. leather scraps, and used leather products). An innovative hybrid technology of processing the secondary waste is presented and tested in industrial conditions and its application on used leather goods is discussed, as well as possibilities of commercial utilization of the products generated by the technology.

Keywords— Hexavalent chromium, spontaneous oxidation, leather waste processing, Raman spectroscopy.

I. INTRODUCTION

CHROMIUM trivalent (CrIII) and hexavalent (CrVI) compounds are produced in large quantities and accessible to most of the population. Salts of CrIII are mainly used as tanning agents during hide processing for stabilization

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of collagen. Elementary chromium is used in alloys in endoprostheses and dentures. CrVI in combination with arsenic and copper (in the form of copper arsenate chromate) are used for preservation of wood products. Chromium is released into the air in large amounts in the form of dust particles during burning of fossil fuels (as Cr³⁺). Other sources are cement plants, municipal waste incinerators, exhaust gases from cars equipped with catalytic converters, emissions from cooling towers using chromium compounds as inhibitors of corrosion, and fly asbestos dust from worn out brake lining (asbestos contains chromium) [1]. Not insignificant amount of chromium is released during seed-cotton roller ginning, where chromium particles are carried into the spun yarns and cotton by-products [2]. Chromium subsequently gets into other parts of the environment by atmospheric deposition. Anthropogenic sources of chromium in water are waste waters from non-ferrous metallurgy, tanning or textile industries, corrosion inhibitors used in cooling systems, hot water distributing or boiler cleaning systems. High concentrations can be found in waters from hydraulic transportation of fly ash. Chromium can be also leached into soil or groundwater from insecure landfills – in this sense, chrome-tanned wastes from tanneries and leather industry represent the highest risk. There are high numbers of these wastes in the areas with former or current massive development of the said industries [3,4].

Chrome-tanned wastes represent long-time threat not only to the environment, but also to the population health. The leather waste comprises:

- a) Tannery waste – liquid and solid (chromium splits, trims, shavings).
- b) Manipulation waste – e.g. leather scraps.
- c) Used leather goods (old shoes, upholstery, etc.).

Processing of the first group of wastes has been successfully solved and is described in several publications [4], including mathematical models for its optimization [5] and computer applications for its automatic control [6]. Another problem is manipulation waste generated during leather goods production, particularly footwear. Besides chromium, this waste also contains fillers, lubricants, dyes and synthetic resins, mainly polyurethanes and polyacrylates. We dealt with these wastes

within the US-Asia Environmental Partnership program in Vietnam for the needs of the NIKE Inc. and the results were published e.g. in [7]. The last and still unsolved problem is the issue of used leather goods. This waste is usually a part of municipal waste and as such it is dumped or incinerated. However, relatively high chromium content makes this waste potentially hazardous. Its combustion produces besides nitrogen oxides also carcinogenic hexavalent chromium compounds. Also disposal of this waste in landfills is related to the risk of uncontrolled oxidation of trivalent chromium CrIII to CrVI.

We have developed a hybrid technology that is able to process even the latter kind of waste. The key part of the technology is mechanical separation of chrome-tanned collagen mass from the non-collagen additives.

Together with the development of the technology, our research is also focused on the precise detection of very low concentrations of CrVI not only in waste leather goods, but also in the still used ones. The analytical methods can also serve for determination of both CrII and CrVI concentrations in landfills or drinking waste sources where chromium can be washed out due to climatic conditions. Measuring only the total concentration of a particular element in environmental or clinical samples can often lead to errors in assessing toxicity, mobility, and bioavailability, as these effects can differ greatly between the various chemical species in which an element may occur [8].

Low concentrations of chromium were measured in [8] with the use of inductively coupled plasma mass spectrometry (ICP-MS) coupled to a liquid chromatography (LC) system in mineral water. The authors of [9] detected CrVI and CrIII concentrations in sea water by flame atomic-absorption spectrometry. This method was also recommended for determination of CrVI and CrIII in tannery effluents. In [10] is described a method for detection of CrVI compounds in air and at workplaces by differential pulse polarography (DPP). A differential pulse polarographic method was also used for detection of CrVI in environmental and soil samples [11]. The authors of [12] in their paper reported the ability of distinguishing CrIII from CrVI with the use of Raman spectroscopy in electrical and electronic equipment. The Raman spectroscopy so far seems a promising method to detect CrVI in samples of various natures. For this reason, we are working at development of a precise analytical method of CrVI detection with the use of Raman spectroscopy.

In this contribution we deal with an innovative technology of processing used leather goods including the possibilities of industrial application of the products. We also present preliminary results from detection of CrVI in leather samples with the use of Raman spectroscopy.

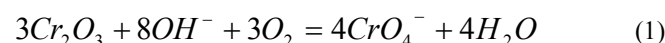
II. THEORY

A. Spontaneous oxidation of CrIII to CrVI

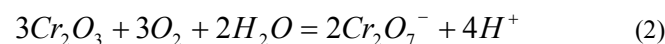
The toxicity of the two oxidation states of chromium is completely different. While Cr³⁺ belongs among essential

trace elements in mammalian metabolism, compounds of Cr⁶⁺ are highly toxic. The primary routes of entry into human body are inhalation, ingestion and skin penetration. The latter route is the most significant. Most CrVI compounds are easily absorbed through the skin [13], are more easily soluble than CrIII in the pH range 5-7, and react with cell membranes.

They can cause dermatitis, often connected with lesions [14]. The greatest risk, however, lies in the fact that reactions of CrVI compounds with cell membranes can lead to kidney and urinary tract carcinomas [13, 15]. The publication [16] also points out an alarming increase in oncological diseases of kidney and urinary tract in the Czech Republic, which may be connected with wearing shoes on bare feet and the increasing import of relatively cheap footwear to the country. The basic question is the possible oxidation reaction from CrIII to CrVI. In basic solutions, the oxidation of CrIII to CrVI by oxidants such as peroxides and hypohalide occurs with ease [13]. Such strong oxidation conditions are realized in the process of the sterilization of drinking water. Another problem concerns the possibility of oxidation of CrIII into CrVI in gentle conditions by air in the wide range of pH:



for alkali medium, and



for acid medium.

The published thermodynamics functions (Gibbs energies of formation) are shown in Table I [17]:

Table I Gibbs free energy of reaction components.

Reaction Component	Change of Gibbs free Energy ΔG (kJ.mol ⁻¹)
Cr ₂ O ₃	-1053.00
OH ⁻	-157.28
O ₂	0.00
CrO ₄ ²⁻	-727.85
H ₂ O	-228.61
Cr ₂ O ₇ ²⁻	-1301.20
H ⁺	0.00

Spontaneous oxidation of CrIII into CrVI is possible within a wide range of pH as shown by the Gibbs Energy values for both reactions:

$$\Delta G_f^0 = -4 \times 727.85 - 4 \times 228.61 - (2 \times 1053 - 8 \times 157.28) = -459 \text{ kJ}$$

for alkali medium, and

$$\Delta G^{\circ} = -2 \times 1301.2 - (2 \times 1053 - 2 \times 228.61) =$$

$$= -22.12 \text{ kJ}$$

for acid medium.

The negative values of both thermodynamic functions prove the possibility of spontaneous oxidation within a wide range of pH. This fact is more dangerous than in the previous case because we do not know under which conditions CrIII may be converted into CrVI.

B. Raman spectroscopy

Raman spectroscopy is an innovative analytical tool with the potential to answer many questions related to chemical details of molecular structure what makes this technique definitely proper for material identification.

Raman spectroscopy is based on so called Raman scattering. Raman scattering is an inelastic scattering of a photon on a molecule. Inelastic scattered photons have slightly changed wavelengths. These changes are characteristic for concrete bonds in surveyed material. The fundamental phenomenon was discovered almost 85 years ago, but its effective use in Raman spectroscopy occurs in about last decade. This revival of the method goes hand in hand with advances in technology: powerful lasers as sources of monochromatic light, efficient Notch filters transmitting all the wavelengths except the excitation wavelength of the laser, sensitive detectors and last but not least computer technology.

Raman spectroscopy has recently proved progressive benefits and become an effective research technique which finds applications across the science disciplines and technical branches. Prime advantages as non-destructiveness, rapidity, contactless measurements or no special requirements for sample preparation makes this method attractive, convenient and effective. Raman spectroscopy also grants highly specific chemical "fingerprint". Every single chemical element, its modification or chemical compound gives rise to a different and unique Raman spectrum via different vibrational behavior. Raman spectrum is then the key for the material identification.

The basic principle of Raman spectroscopy is depicted in Fig. 1 [18]. Raman spectroscopy has many advantages. The method is:

- non-destructive what allows undergoing investigated samples further analyses or simply repeat Raman analyses.
- relatively rapid, Raman spectra can be acquired in a few seconds.
- contactless what is convenient, samples are not contaminated, also it is advantageous when toxic, dangerous samples or those with strong aroma are measured. There also exists a possibility of measuring samples through transparent glass or polymeric covering layers or containers. Raman spectra of the covered sample and the cover can be then subtracted via software.
- applicable to all states of matter and different its forms (crystals, powders, fibers, solutions, etc.) .
- without special requirements for sample preparation, what is

convenient and prompt.

- usable as in situ analysis.

Connecting a microscope to a Raman spectrometer, conveniences of optical microscopy extends usability and versatility of such an instrument. The amount of samples required for analysis is reduced to the order of micrometers, trace amounts of samples can be analyzed, the availability for the purposes of the selective analyses of components are more precise. Considering limitations of the method, the greatest one is the possible appearance of undesirable phenomenon fluorescence. Raman scattering is a weak effect, approximately only one of 10^7 of incident photons is scattered in inelastic way. Fluorescence as a stronger quantum effect can mask the Raman bands or even make it impossible to obtain Raman spectra. Typically biological samples exhibit a high level of fluorescence which can be suppressed using laser with less energy laser, usually from the (near) infrared region. Another advantage can be a thermal degradation of the sensitive sample when using a high power of the laser. Not all the compounds of interest are already available in spectral databases and libraries, but they are developed.

Above mentioned ability makes Raman spectroscopy possible to distinguish between the trivalent and hexavalent chromium on principle. [12] Also other valences of chromium compounds include differences in Raman spectra [19].

III. EXPERIMENTAL

A. Determination of Cr spectra in leather sample

A sample of chrome-tanned leather was merged into a solution of chromium bichromate to contain detectable amount of both forms of chromium. Raman spectra of leather containing chromium compounds were recorded using Renishaw InVia Basis Raman microscope equipped with two lasers: argon ion laser with the excitation wavelength 514 nm and laser maximum output power of 20 mW and near-IR diode laser with the excitation wavelength 875 nm and laser maximum output power of 300 mW. Leica DM 2500 confocal microscope with the resolution up to 2 μm was coupled to the Raman spectrometer. Measurement parameters for obtaining Raman spectra were 20 s exposure time, 10 accumulations, laser power 10 mW and the spectral range 100 – 3200 cm^{-1} . Spectrum of hexavalent chromium was obtained from a leather fiber using the same method as described above.

B. Industrial tests of the processing technology

We carried out industrial scale trial using NIKE leather scraps as the input raw material. This technology is also suitable for the processing of used leather goods, especially old shoes, with the preceding separation of leather and synthetic part. The separated parts are subsequently subjected to mechanical crushing to facilitate their further processing. The leather part is then treated according to the following scheme (Table II):

Table II Consecutive steps of the industrial trial.

Destruction of surface resins
Alkaline saponification of fats
Neutralization
Enzymatic hydrolysis at pH 9 catalyzed by ALCALASE DX-L
Neutralization at pH 5.7
Converting emulsion to a suspension
Careful filtration (critical step)
Separation of protein solution from hydrated chromium, titanium hydroxides

A stirring reactor with total load capacity 17 tons of reaction mixture was used. The batch of reaction mixture was the following: 300 kg of NLS (NIKE Leather Scrap), 60 kg of pure potassium hydroxide and 5,940 kg of technological water (without chlorine). The industrial trial was carried out in the KORTAN Company, Hradek nad Nisou, Czech Republic. The detailed description of the industrial test is given in Table III.

Table III The course of the industrial experiment.

Total time (hours)	Temperature (°C)	pH	Note
0	12	6.4	Loading of 5,940 kg water
0.58	12	6.4	Beginning of KOH dissolving
0.75	15	14	End of KOH dissolving
0.83	15	-	Beginning of 300 kg NLS dosing
1	15	-	End of 300 kg NLS dosing
1.25	15	-	Beginning of reactor heating
2.75	70	12	Optimum temperature achievement
5.75	69	-	Addition of 30 kg HNO ₃ 65% p.a.
5.9	73	9.9	Addition of 5 kg HNO ₃ 65% p.a.
6	74	8.94	-
6.1	74	8.9	Addition of 2.5 kg ALCALASE enzyme
7	73	8.9	Test of filtration – very

			slow
9	72	-	Stopping of steam supply
10	70	-	Stopping of stirring
	The reaction continued the next day		
23	57	6.5	Gradual addition of 19 kg phosphoric acid p.a. 85%
24	65	6.5	Taking of 400 kg heterogeneous reaction mixture on filter
26	70	6.5	End of 400 kg heterogeneous mixture filtration
26.5	70	5.73	Gradual addition of 3 kg HNO ₃ 60% p.a.
27	68	5.73	
34	65	5.73	Gradual filtration (four times) nest 3,700kg of mixture
35	61	5.73	Gravimetric filtration during the night. Filtration of 2,200 kg mixture

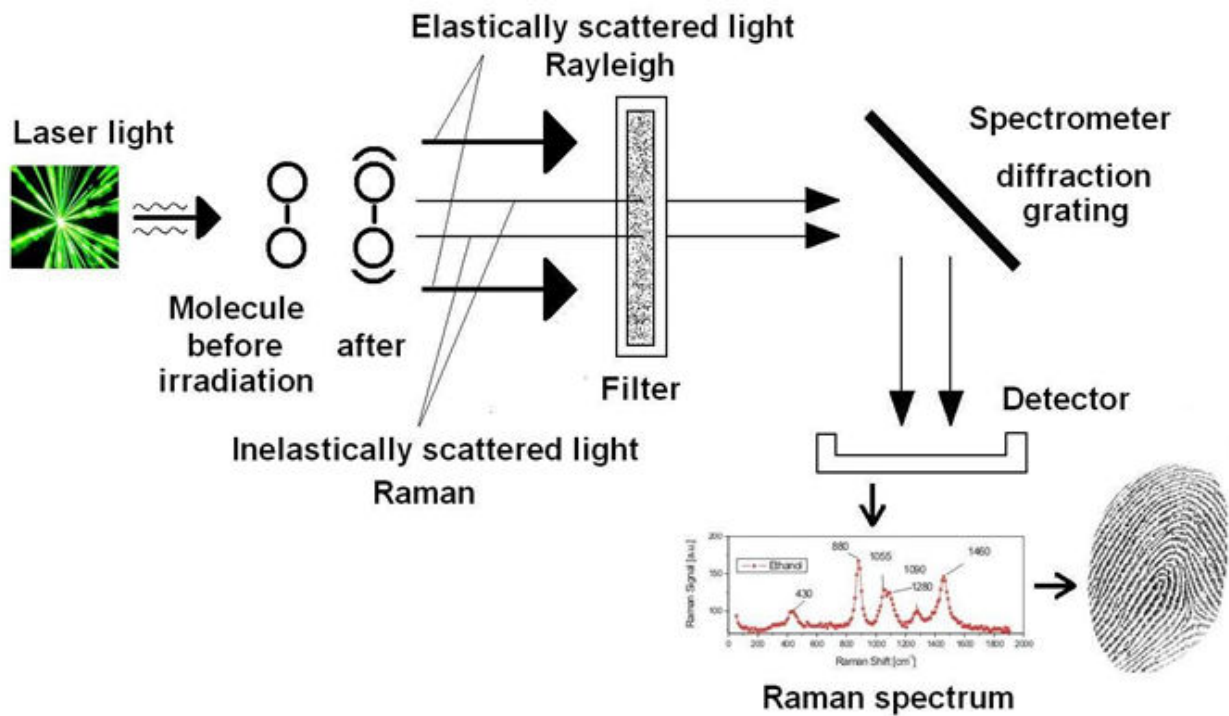


Fig. 1 Principle of Raman spectroscopy. The sample is irradiated with laser, molecule vibrates, filter eliminates intense Rayleigh scattering, and the grating disperses the light onto a detector to generate a spectrum, which gives the information about molecule bonding.

IV. RESULTS AND DISCUSSION

A. Chrome-tanned waste processing technology

The first part of our paper deals with the still topical need for economical and environmentally friendly processing of chrome tanned leather waste. We particularly focus on manipulation waste generated during processing leather into the final products of leather industry and used leather goods such as old shoes, but the technology is able to process all kinds of tannery and leather waste, as can be seen in Fig. 2.

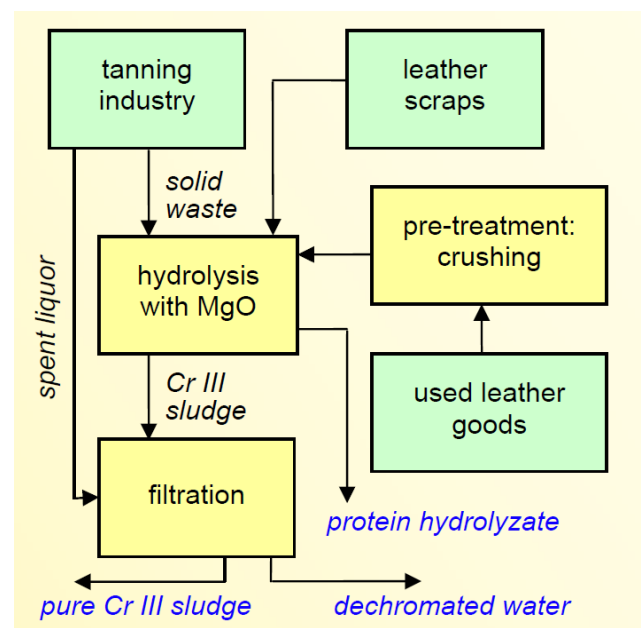


Fig. 2 Simplified scheme of the complex technology of processing tannery and leather wastes.

Although there are some companies [e.g. 21] focusing on collection and re-use of waste textiles, there is no worldwide collection and processing technology for used leather goods, especially old shoes. Our research was based on our long-term

experience with the processing of manipulation leather waste. This technology lies in several steps the first of which is a mechanical separation of the collagenous part containing chromium from the non-collagenous additives (such as vulcanized rubber in the soles or other synthetic components). In the second step, the separated parts are subjected to disintegration which facilitates their further processing. The next steps concern hydrolysis of the collagenous part to a soluble collagen hydrolyzate and insoluble part the main component of which is hydrated chromium oxide (so called chromium sludge).

The industrial tests of the technology gave the following

products: 5,500 kg of filtrate with dry matter content 4.5% and 900 kg of filter cake. The filter cake was freely dried and the filtrate was concentrated in the vacuum evaporator to the dry matter content of 22%. The concentrated protein hydrolyzate (NPK – organic fertilizer) was dried in the fluidization dryer and 130 kg of dry hydrolyzate was obtained. Especially the filtrate seems to be economically very interesting. Due to the addition of potassium hydroxide and phosphoric acid during the hybrid process, the concentrated and dried filtrate represents a good quality NPK fertilizer.

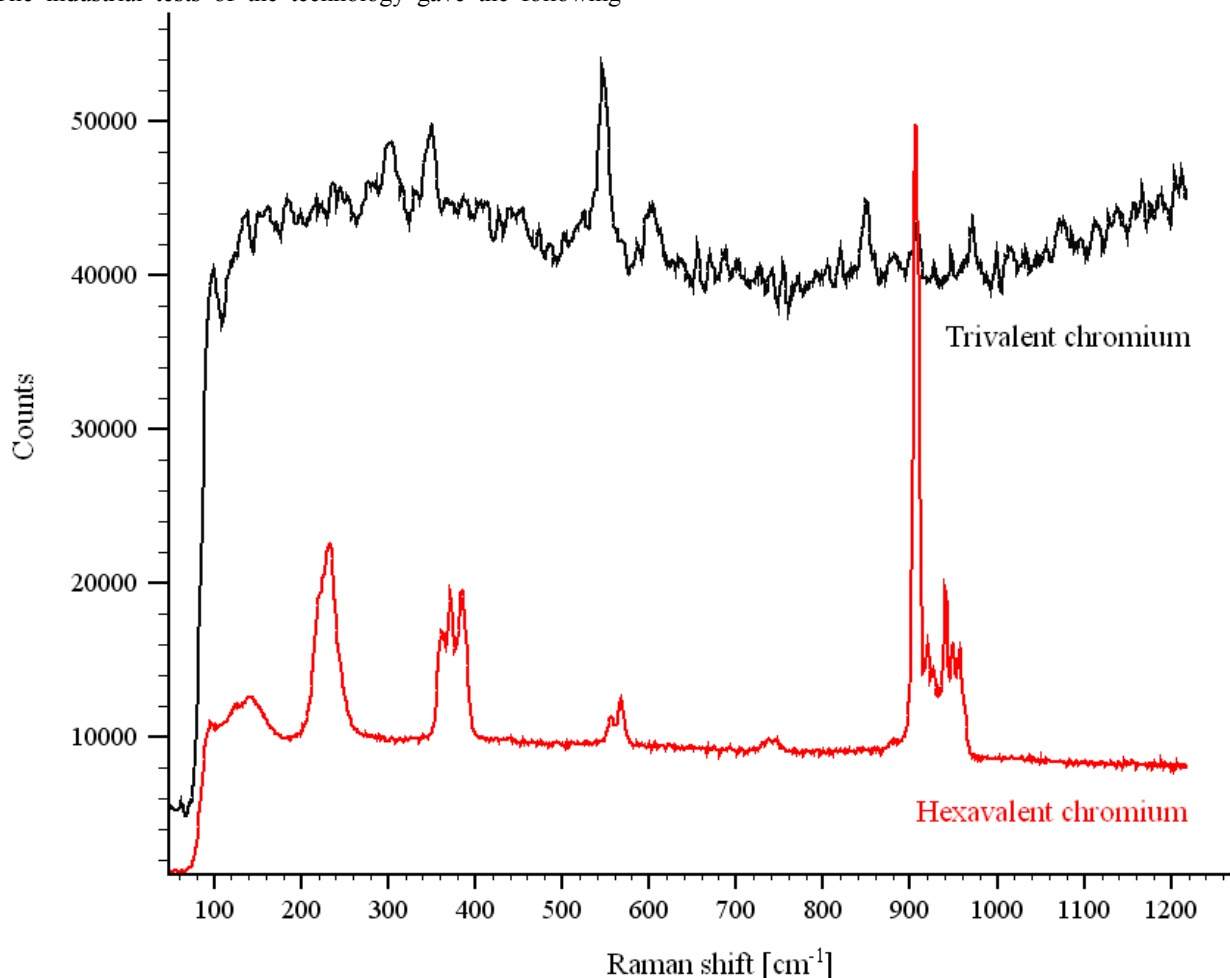


Fig. 3 Raman spectra of trivalent and hexavalent chromium in leather sample.

In addition to the manipulation waste, the hybrid technology seems to be an effective solution also for used leather products, e.g. old shoes. These goods, especially those in which the chromium content is not carefully controlled, represent potentially hazardous waste in the same way like chrome shavings or leather scraps and should not end up in municipal waste. The authors propose selective collection (like it is already done with paper, plastics, glass and metals) of these used products. After crushing, the hydrolysable parts can be processed by the above mentioned hybrid technology. The

processing of the other part, which cannot be hydrolyzed, is a subject of intensive research. According to preliminary results, pyrolysis of the non-collagen parts seems to be an effective way, with a focus on products applicable as liquid fuels.

B. Detection of CrIII and CrVI by Raman spectroscopy

The other part of the paper is focused on detection of CrIII and CrVI, especially in leather samples. Fig. 3 shows the Raman spectra of trivalent and hexavalent chromium from leather sample, Fig. 4 shows spectrum of hexavalent chromium

obtained from a leather fiber.

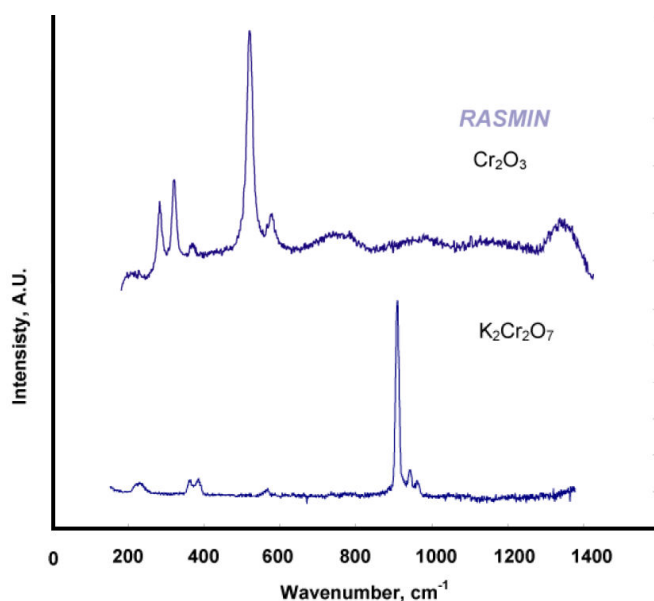


Fig. 5 Raman spectra of trivalent and hexavalent chromium available from the Raman spectral database [21].

The spectra of both forms show obvious differences. The presence of hexavalent chromium affects the dominant peak at 911 cm^{-1} in the spectrum; from lower wave numbers there are characteristic bands at 231 cm^{-1} , at $350\text{--}400\text{ cm}^{-1}$ and also around 864 cm^{-1} . Raman spectra of trivalent chromium feature two bands in the region from $300\text{--}350\text{ cm}^{-1}$ and the peak at 541 cm^{-1} . Fig. 5 reveals Raman spectra of trivalent and hexavalent chromium available from the Raman spectral database [21]. Chromium compounds are generally fairly well measurable with excitation in visible region.

However, acquired spectra showed the complication with luminescence of the leather when using visible light Ar^+ laser. More suitable for detecting chromium compounds in leather is less energetic near infrared laser which provides much better and clearer spectra. The essential fact is that Raman spectroscopy can be used for the evaluation of the presence of chromium compounds in leather. There are very few reports on analytical methods for the detection of CrVI traces in leather samples, especially used leather goods, or the behavior of chromium compounds in various conditions (e.g. the micro-environment in the contact area of a bare foot and footwear). Some attempts have been published in [22], where automobile leather samples were artificially aged by using temperature and temperature + UV radiation aging factors. After artificial aging process, chromic oxide, soluble matter in dichloromethane, chromium (VI) and formaldehyde contents in the leather were analyzed to determine chemical decomposition and findings compared with values before the aging process. Besides, the alteration of leather structure was investigated by Raman Spectroscopy. Increase of CrVI and formaldehyde contents and decrease of chromic oxide and soluble matter in

dichloromethane contents were determined in finished automobile leather samples after the ageing process.

This supports our theory that used leather goods represent a potential threat to its users and the environment, especially when directly exposed to climatic conditions. In the near future, we plan to develop a more precise analytical method for the detection of very low CrIII and CrVI concentrations to determine the conditions for the prevention of spontaneous oxidation.

V. CONCLUSION

This study concerns the potential health risks of hexavalent chromium in the waste generated by leather industry and the possibilities of economical and environmentally friendly processing of this waste. Possibility of spontaneous oxidation of CrIII present in leather wastes and goods to CrVI is discussed. Preliminary results are presented from analytical detection of low concentrations of chromium in leather samples using Raman spectroscopy. Precise detection of low concentrations of particularly hexavalent chromium is the key step for further research – determination of the conditions under which the spontaneous oxidation can occur. A new three-step hybrid technology of processing manipulation waste is proposed and tested under industrial conditions. The filtrate obtained by this technology can be used in agriculture as a good quality NP or NPK fertilizer. The solid product can serve as an inorganic pigment in glass and ceramic industry. The technology also seems to be an effective solution for hydrolysable parts of used leather products, e.g. old shoes.

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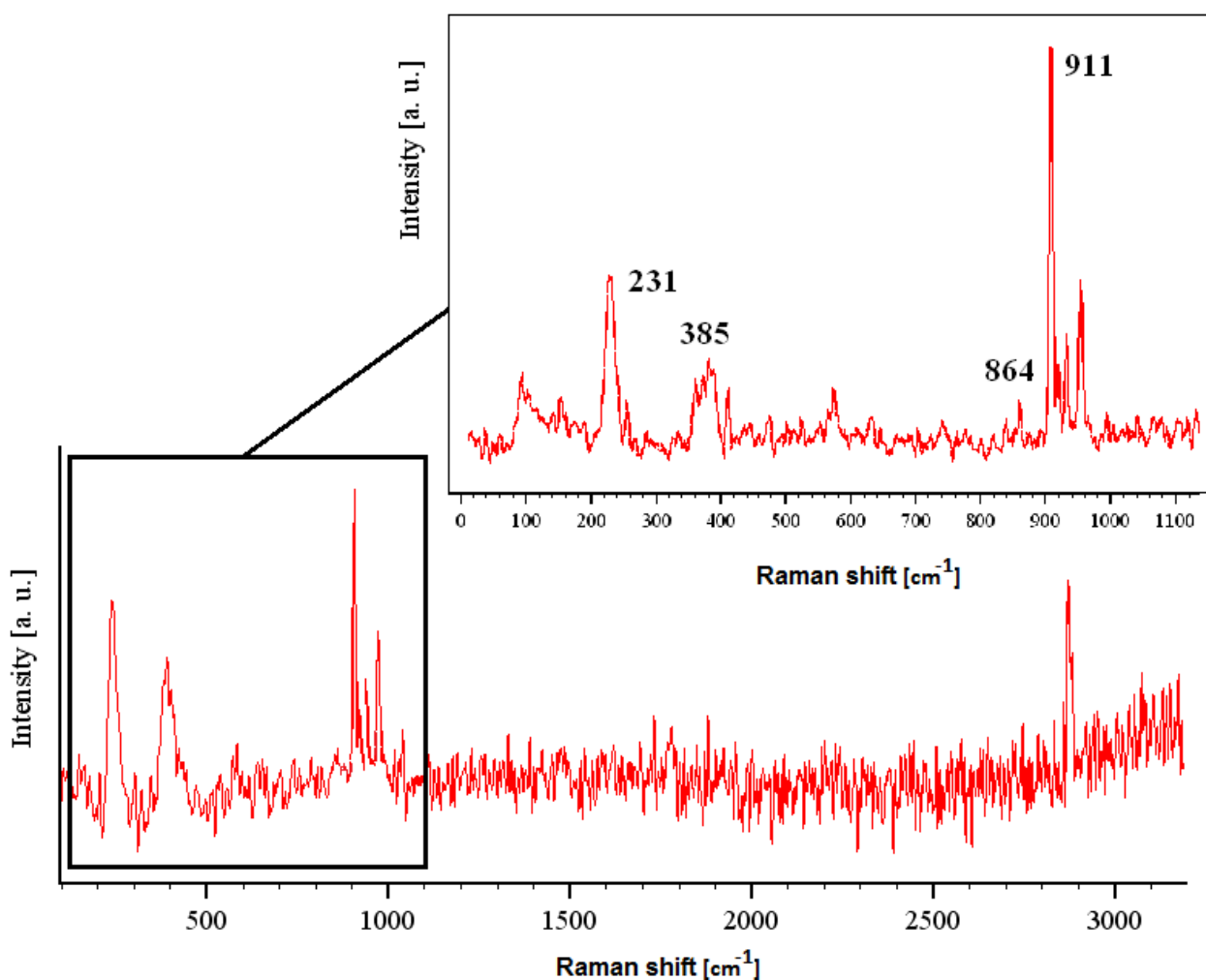


Fig. 4 Raman spectrum of hexavalent chromium obtained from a leather fiber.

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Karel Kolomazník was born in Kromeriz, May 5, 1938. He took up an academic position in Zlín in 1970 at the Faculty of Technology of Brno University of Technology (which was later changed to Faculty of Technology of Tomas Bata University in Zlín). Since 2006 he has been working at the newly established Faculty of Applied Informatics. His research group deals with optimization of technological processes particularly in the field of processing waste generated by tanning, leather and food processing industries into valuable products.

He has led and participated in many successful projects funded e.g. by the Ministry of Education, Youth and Sports of the Czech Republic, Ministry of Industry and Trade or the Ministry of Agriculture, the Czech Science Foundation, the US-Asia Environmental Partnership program, etc. In addition to that, he has put most of his results into industrial practice in cooperation with commercial partners from both the Czech Republic and abroad. He has had a long-term cooperation with the Eastern Regional Research Center of the U.S. Department of Agriculture, Wyndmoor, PA where he successfully applied the ammonia-free deliming of white hide. In the NIKE Inc. (Ho Chi Minh City, Vietnam) he implemented a patented technology for the processing of manipulation waste from leather industry including the application of the products. He has been also active in industrial applications within the Czech Republic, e.g. implementation of a patented technology of a protein hydrolyzate production from animal-based organic waste in the Kortan, s.r.o. in Hrádek nad Nisou.

Prof. Kolomazník was awarded in 1998 the "Rolex Award for Enterprise", for the technology of processing and recycling of potentially hazardous chrome-tanned waste produced by the leather industry. In 2009 he received the ALSOP Award of the American Leather Chemists Association for his long-term contribution to the association and the leather industry.