Hexavalent Chromium Determination in Waste from Leather Industry Using Spectrophotometric Methods

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Abstract: - Focus of this paper is the description of common used methods for hexavalent chromium measurement. This work is focused especially on commonly available spectrophotometric method based on the reaction with 1,5-diphenylcarbazide, because not every laboratory is equipped with modern devices for this pollutant measurement,. Special attention was focused on the variability possibilities of the basic spectrophotometric method with practical demonstration of individual variants, some critical points and moments in laboratory conditions using real samples containing hexavalent chromium. Among others, there are mentioned other spectrophotometric methods with which we do not meet often. Confirmation of presence of hexavalent chromium in samples was performed also by Raman spectroscopy and use of this method was discussed too.

Key-Words: - Leather waste, hexavalent chromium, measurement variability, spectrophotometric method, 1,5-diphenylcarbazide, Raman spectroscopy.

1 Introduction

Hexavalent chromium belongs to strictly monitored pollutants in the environment and in many industrial branches. The anthropogenic sources of chromium include wastewaters from metallurgy, metal coatings, leather and textile industries, etc. From several oxidation states in which chromium can exist, the trivalent and hexavalent states are the most important from the viewpoint of the environment and commercial applications. These forms differ strongly. Whereas trivalent chromium occurs naturally in the environment and belongs to essential elements important for human body with influence on blood sugar control, hexavalent chromium compounds are toxic, carcinogenic and mutagenic and more soluble and mobile.

One of traditional application areas of chromium compounds is the leather industry. Chromium sulphate is the most popular tanning agent worldwide. This way of tanning gives leather its unique features by means of crosslinking of collagen fibres with chromium bridges. However, leather industry also ranks among major producers of potentially hazardous wastes. The processing of 1000 kg of raw hide into leather results in creating of only 200 kg of final product (leather) with chromium content of 3 kg, 250 kg of non-tanned protein waste, 200 kg of tanned wastes with chromium content of 3 kg, and 50000 kg of waste water containing 5 kg of chromium. [1] It follows from the above mentioned that both products and wastes of the leather industry contain considerable amount of chromium. In the past decades strict environmental regulations have been ordered to limit disposal of tannery waste into soil and water bodies in the developed and developing parts of the world. Before that, this chromium containing waste was mostly landfilled or merely dumped and thus distributed into the environment. [2] Many tanneries have caused severe water pollution in river bodies and thus in ground water with toxic hexavalent chromium. [3] There are many landfills containing this kind of waste worldwide that could be a threat for sources of drinking water and local fauna and flora because it is practically impossible to predict the processes in the landfill body or the state of protection barrier in the next 50 or 100 years. [4]

There are reports in literature that from the thermodynamic point of view there exists a possibility of spontaneous oxidation of trivalent chromium into its hexavalent form. [5] In the process of leather manufacturing this could happen for example during the tanning, post-tanning and finishing operations in the presence of various oxidation agents (e.g. hydroperoxide forming, high thermal conditions, binders, high pH value ...). The

occurrence of chromium species is pH-dependent. Cr(III) is very difficult to oxidize in acid solution owing to the normal reduction potential; in alkali conditions oxidation occurs to form stable chromate. [6] Oxidation could be caused by some oxidation reagents as atmospheric O_2, O_3, UV rays, H_2O_2, peroxocompounds, MnO_2 etc. The natural oxidation of Cr(III) is extremely low, most of Cr(VI) found in soil and groundwater comes from pollution. On the other hand Cr(VI) as chromate CrO_4^{2-} is a strong oxidizing agent and unstable in acid solutions in the presence of organic molecules with oxidizable groups and electron donors as HSO_3^-, Fe^{2+} etc. This fact is exploited by remediation of pollution by $FeSO_4$ or nanoFe^0. [7] Cr(VI) can be produced at low incineration temperatures (300-600°C) which confirms impracticality of the conventional disposal methods for leather waste. [8] Occurrence of both form in waters is described in Fig. 1, which shows the dependence of oxidation/reduction potential E on pH [9].

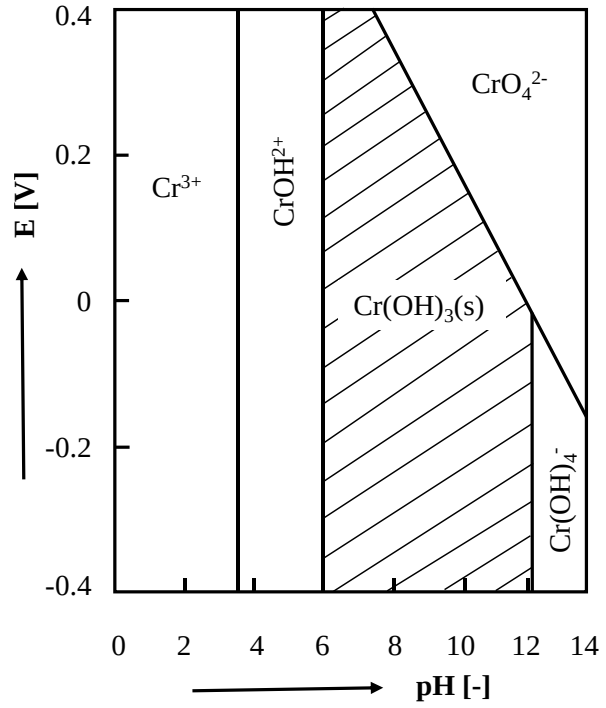

Fig. 1: E-pH diagram of area of prevailing existence of Cr(III)-Cr(VI) system, $c(Cr_{total})$=0,52 mg.L^{-1}, t=25°C.

For the reasons described above and due to high toxicity of Cr(VI) compounds, analytical determination of hexavalent chromium is of great importance not only in relation to the leather industry.

Determination of hexavalent chromium can be performed by various laboratory procedures. Some methods were described long years ago and some use the most sophisticated instrumentation. The overview of used and published methods for various samples and areas of application is described in publication [10]. Very interesting method with a low limit of detection (in the range of μg.L^{-1}) is ion chromatography combined with post column derivatization with diphenylcarbazide and photometric detection used for example for drinking water control. [11], [12] The quickest method is probably Raman spectroscopy. [13] However many technical articles mention basic photometric detection with 1,5-diphenylcarbazide as the main method. This method is very popular due to good sensitivity and feasibility.

Determination of Cr(VI) in leather is carried out for example by international standard [14] using diphenylcarbazide method and in waste using numerous EPA methods. However, many articles mention only the utilization of "method with diphenylcarbazide at wavelength 540 nm", without any description of the steps between the sample preparation and the final chromium content. The diphenylcarbazide method could be performed with various modifications.

The aim of this article is to provide an overview of modifications in diphenylcarbazide method together with useful information on practical Cr(VI) determination based on the international standard and laboratory experience using real samples of leather waste.

This paper contains knowledges about chromium in leather industry, descriptions of common and less common methods for hexavalent chromium determination and the practical demonstration of diphenylcarbazide method variability.

2 Spectrophotometric Methods and Spectroscopic Methods

2.1 Determination with 1,5-diphenylcarbazide

Cr(VI) in solution oxidizes 1,5-diphenylcarbazide to 1,5-diphenylcarbazone in a mineral acid environment to give a red-violet complex with chromium. Absorbance of this complex is measured mostly at the wavelength of 540 nm (maximum of the complex) or close to this value (546, 550 or 555 nm). Phosphoric or sulfuric acids are used to create the acidic conditions. Maximal coloration is achieved after 1 min. and the stability is minimally 30 min. Absorbance is measured after 15±5 min.

The reagent is prepared by dissolving 1,5-diphenylcarbazide in ethanol (0.25 g + 4 g phthalic acid anhydride in 100 mL) or in acetone (0.5%, 1% solution). [15]

2.2 Determination Using CdI_2 and Starch

The reagent is prepared by dissolving 1.1 g of CdI_2 in 34 mL of water and the mixture is boiled to remove free I_2; 0.26 g of starch is dissolved in 46 mL of water under boiling and both solutions are mixed under gentle boiling, filtered using glass frit, cooled and filled to the mark in a 100 mL volumetric flask. The prepared reagent is protected from direct sunlight. A total of 2.2 mL of 0.815M H_2SO_4 is added to a 1 mL of solution containing 0.5-5 μg Cr(VI), then water is added till the total volume of the mixture is 9 mL, and finally 1 mL of the reagent. Absorbance of blue starch-iodine complex is measured after 20 min at a wavelength of 575 nm. [15] The method presented here covers the range 0.05 to 0.5 μg. of hexavalent chromium per mL in a final volume of 10 mL as described in publication [16].

2.3 Other Methods

Of the others method it could be mentioned the spectrophotometric determination of Cr(VI) ions using new benzothiazolyl azo compound 2-[(6-methyl-2benzothiazolyl) azo]-4-chlorophenol. This method is sensitive, selective and rapid and it allows the determination of Cr(VI) in the range of 0.2-9.0 $mg.L^{-1}$. The absorbance of the resultant solution remains stable for over 20 hours. Details of procedure are described in publication [17].

These methods are only mentioned for the sake of completeness of spectrophotometric determination, but were not in the center of interest of this paper.

2.4 Alkaline Extraction of Cr(VI)

The extraction of Cr(VI) from waste samples is carried up under alkali conditions in order to eliminate the to Cr(III). One procedure is described in the following chapter. Literature sources mention the extraction using hot solution of a mixture of 3% $NaCO_3$ and 2% NaOH. The amount of 100 g of solid waste is mixed in a beaker with 400 mL of the extraction solution and the mixture is heated under constant stirring closely under the boiling point. After cooling and filtration the pH of the solution is adjusted under stirring with concentrated nitric acid into a range of 7-8. The solution is then filled to the mark in a 1000 mL volumetric flask with deionized water and the content of Cr(VI) is measured. [18] In publication [19] is practical comparison of mentioned alkali extraction with acid extraction using 0.2M H_3PO_4 from soil and sediment samples and following determination of Cr(VI) using method with 1,5-diphenylcarbazide and AAS.

2.5 Raman Spectroscopy

Raman spectroscopy/microscopy has recently become an effective research technique finding applications across the science disciplines. Progressive benefits of Raman spectroscopy made the method proper for material identification, molecular bonding studies and structural changes investigations. 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 – the key for the identification. Method is based on inelastic scattering of the monochromatic light on molecules. The basic principle of Raman spectroscopy measurements is described in Fig. 2.

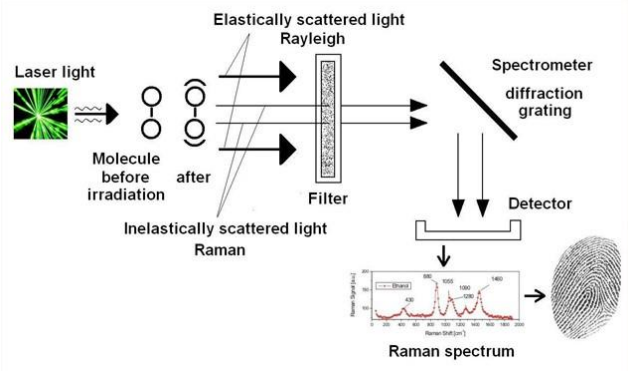

Fig. 2: The sample is irradiated by laser, molecule vibrates, filter eliminates intense Rayleigh (elastically) scattered light, the grating disperses light onto a CCD detector do generate Raman spectrum which gives information about a molecule bonding and provides a chemical fingerprint for identification.

Advantages of the method plays important role also in analysis of products of leather industry:

Due to specific chemical fingerprint of the substance it is possible to distinguish the valence of chromium – especially trivalent and hexavalent form, what arise from the principle of the method and is experimentally proved, too. [13], [20] Raman spectra of CrIII and CrVI compounds show diversity as are displayed in Fig. 3. Compounds of Cr(VI) have most intensive characteristic peak at 907 cm^{-1}, compounds of Cr(III) at 554 cm^{-1}.

Non-destructivity guarantees no disruption of the sample and possibility to return the leather product back into use after analyses.

Contactless measurements allow analyses through transparent covering layers and packaging, thus safe measurements of hazardous and toxic materials or substances with a strong aroma.

Samples do not require to be anyhow prepared for the measurement. No chemical reagents and agents are needful, what prevent additional chemical reactions. That is safer and structure of samples is not affected/altered.

Rapidity is an important advantage over many conventional laboratory techniques. Raman spectra can be acquired already within seconds.

Applicability to aqueous solutions enables beside leather products to analyse the content of chromium e.g. in wastewater.

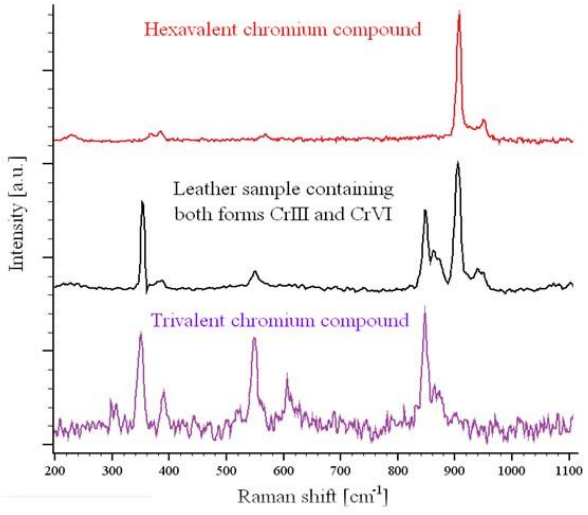

Fig. 3: Raman spectra of leather containing Cr(III) and Cr(VI) compounds.

In spite of the fact, that the particularity of Raman spectroscopy is remarkable, the conversion efficiency of Raman effect is rather poor, since only a scarcity (about 10^{-7}) of the initial photons are scattered on molecules in inelastically. Hence the detection of very low concentrated molecules can be limited. Another drawback is the occurrence of luminescence effect from some materials that partly cover or even totally masks the less intense Raman spectra. Luminescence activity commonly occurs in the biological samples, including also the leather. However, there exist several manners to reduce or eliminate luminescence, e.g. to use laser from NIR area.

3 Materials and Methods

The determination of Cr(VI) was carried out using real samples of cattle hide shavings, tanned sheep leather trimmings and the hydrolysate from alkali enzymatic hydrolysis of leather shavings derived from boar skins.

The reagents, calibration solutions and phosphate buffer were prepared from the following commonly available laboratory chemicals: acetone, argon, glacial acetic acid, 1,5-diphenylcarbazide, H_2SO_4, H_3PO_4, $K_2Cr_2O_7$, $Na_2HPO_4x12H_2O$.

The spectrophotometric measurements were performed using Spekol 11 (Carl Zeiss, Germany) with extension for 1 cm and 5 cm cuvettes.

The reagent was prepared by dissolving 1 g of 1,5-diphenylcarbazide in 100 mL of acetone and acidified with one drop of glacial acetic acid.

Distilled water was boiled and cooled to degas (it is possible to use an ultrasonic bath at the end of the buffer preparation).

The phosphoric acid solution was prepared by diluting of 0.7 L of phosphoric acid (w=85 %) to a 1 L flask with distilled water.

The phosphate buffer was prepared as 0.1M solution of $Na_2HPO_4x12H_2O$ with pH adjusted to 8 using said phosphoric acid solution and finally the buffer was degassed by argon.

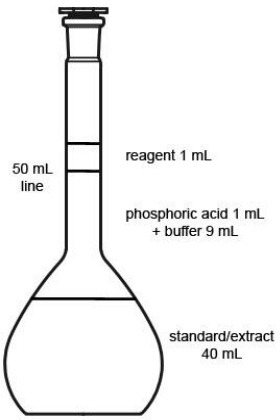

Fig. 4: Composition of the volumetric flask before

coloration.

The calibration standards were prepared by consecutive diluting of a 1000 mg.L^{-1} Cr(VI) stock solution. Final dilution was performed with phosphate buffer. The volume of sample in a 50 mL volumetric flask was 40 mL; the rest of space was intended for acid, buffer and reagent (Fig. 4).

The Cr(VI) extraction from the samples was performed using laboratory horizontal shaker and closeable bottles. Almost no free space was left at the top of the bottle. The ratio between the solid sample and phosphate buffer was approximately 2-3 g for 100 mL of buffer. The shaking time was 3 hours. The pH value of the mixture should not change. After that the mixture was filtered using a paper filter for slow filtration and the obtained filtrate was filtered one more time through a syringe filter (0.22 and 0.45 μm).

A volume of 40 mL of the extract/calibration standard was transferred into a 50 mL volumetric flask, 1 mL of phosphoric acid was added and phosphate buffer was made up to a volume of 50 mL. After that, 1 mL of the reagent was added, unlike the common practice and the standard, above the 50 mL line and the mixture was well stirred. Using this way it is possible to add the reagent almost in one moment into all volumetric flasks. The absorbance was measured after 20 min. at the wavelength of 540 nm against a blank sample prepared from the phosphate buffer, phosphoric acid and the reagent using cuvettes with optical length of 5 cm.

The easiest procedure includes the following steps. To the solution containing Cr(VI) in a volume of 40 mL is added sulfuric acid for pH adjustment into a range of 1±0.3. In our case, 0.5 mL of concentrated sulfuric acid was added. This solution is transfered into a 50 mL volumetric flask and distilled water was added to the mark. After that, 1 mL of the reagent was added above the 50 mL line and the mixture was stirred well. The absorbance was measured after 20 min. at the wavelength of 540 nm against a blank sample prepared from distilled water, sulfuric acid and the reagent using cuvettes with optical length of 1 and 5 cm.

An InVia Basis Raman microscope (Renishaw) was used for the recording of the Raman spectra of collagen hydrolysate. A NIR diode laser with the excitation wavelength 785 nm and a maximum output power of 300 mW was used as the light source. A Leica DM 2500 confocal microscope with the resolution up to 2 μm was coupled to the Raman spectrometer. The measurements were collected at 20x magnification, with 1 second exposure time and 100 accumulations. The sample was scanned in the range from 500 to 1600 cm^{-1} with a 2 cm^{-1} spectral resolution. To avoid any interference, the Raman spectra were acquired in the absence of light. The baseline correction was applied.

4 Results and Discussion

4.1 Basic Procedure with Sulfuric Acid

In this case, the easiest procedure was performed to find out the response of the device and the limit of quantification. The measurements of the solutions were carried out using cuvettes with optical length of 1 and 5 cm. Calibration solutions were prepared in the range of 0.01-3 mg.L^{-1} Cr(VI). However, the response of the spectrophotometer especially for low concentrations was weak - on the second and third decimal place.

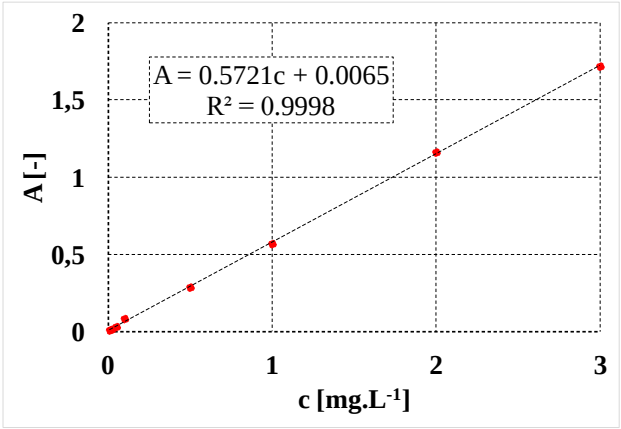

Fig. 5: Basic procedure - calibration curve for 1 cm cuvette.

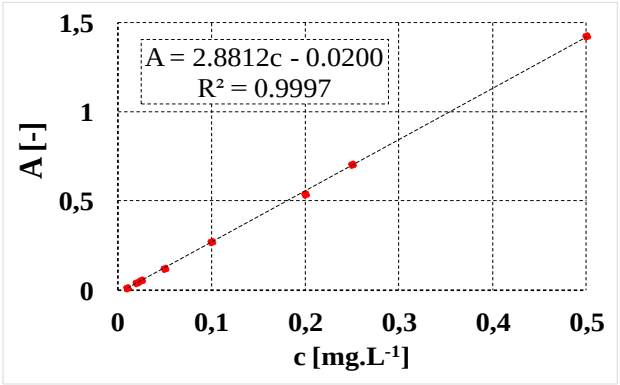

Fig. 6: Basic procedure - calibration curve for 5 cm cuvette.

The measurement was repeated using the cuvette with higher optical length of 5 cm to achieve better results for low concentrations. The difference is evident comparing Fig. 5 and Fig. 6. The Lambert-Beer law is valid – the slopes of the curves are in the same ratio as the cuvette lengths. The highest point of the curve was due to the high response at a concentration of 0.5 $mg.L^{-1}$. However the response for a concentration of 0.01 $mg.L^{-1}$ was weak again, so the authors recommend not to use this method for measuring Cr(VI) concentrations under 0.02 $mg.L^{-1}$.

4.2 Procedure using Phosphate Buffer

The phosphate buffer was used for the extraction of real samples and for calibration solution preparation. The measurements were carried out with a cuvette with optical length of 5 cm. The resulting calibration curve is shown in Fig. 4. It is interesting that the response is twice as high compared to the basic procedure (Fig. 7). The selected picture represents one of many other measurements. According to high values of absorbance by last calibration points the range was narrowed to 0.01-0.25 $mg.L^{-1}$. The use of the lowest point is questionable and the aforementioned recommendation is valid.

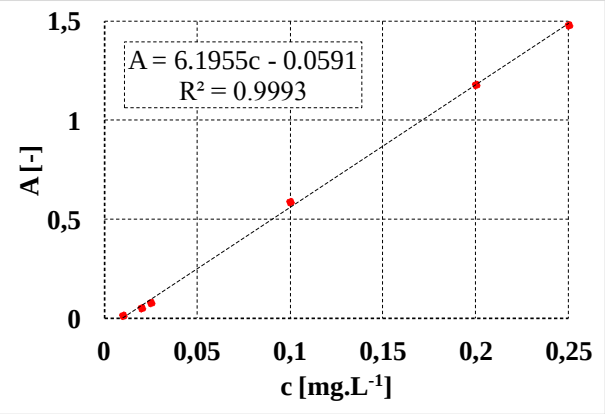

Fig. 7: Procedure using phosphate buffer - calibration curve for 5 cm cuvette.

Extracts from solid samples were in the case of second filtration a) non-filtered, b) filtered using a syringe filter of 0.45 µm or c) filtered using a syringe filter of 0.2 µm. During the first filtration, residual turbidity or some small particles can influence the measurement and the second filtration stage should be applied.

According to the results in the case of chromium shavings we can see small difference between the non-filtered and filtered extracts as shown in Table I, all extracts were clear. Hexavalent chromium occurred in small concentration.

But influence of the turbidity occurred by non-filtered extract from trimmings and caused difference between results (Table II). The turbidity was almost invisible by eye. The second stage of filtration was necessary and the Cr(VI) concentrations by filtered extracts are comparable. In this sample, hexavalent chromium was also detected.

A syringe filter or a comparable filtration using similar filter can remove the substances which could affect the measurement.

Table I: Results related to cattle hide shavings.

parameter	unit	cattle hide shavings		
dry mass	%	71.8		
sample weight	g	3.10	2.99	3.20
Cr(VI) concentration	$mg.L^{-1}$	0.036	0.035	0.036
Cr(VI) content in dry mass	$mg.kg^{-1}$	**1.61**	**1.65**	**1.55**
2nd stage filtration		none	0.45 µm	0.2 µm

Table II: Results related to tanned sheep leather trimmings.

parameter	unit	tanned sheep leather trimmings		
dry mass	%	89.6		
sample weight	g	3.11	3.10	3.13
Cr(VI) concentration	$mg.L^{-1}$	0.049	0.013	0.014
Cr(VI) content in dry mass	$mg.kg^{-1}$	**1.74**	**0.47**	**0.50**
2nd stage filtration		none	0.45 µm	0.2 µm

4.3 Measurement Using Raman Spectroscopy

The content of Cr(VI) was measured in the hydrolysate obtained from alkali enzymatic hydrolysis of leather shavings derived from boar skins. Raman spectroscopy was used for qualitative measurements and the diphenylcarbazide-based method was used for quantitative measurement. As can be seen in Fig. 8, the Raman spectrum showed the presence of Cr(VI).

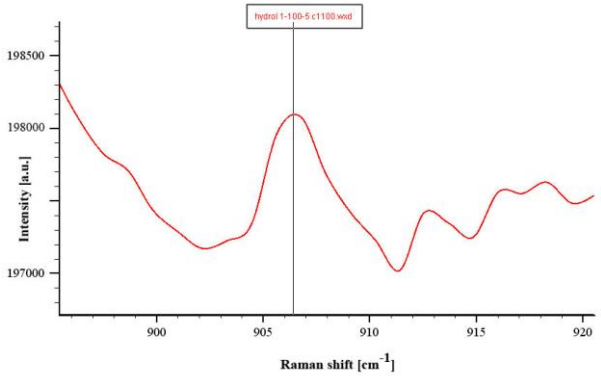

Fig. 8: Raman spectrum of dry collagen hydrolysate - detail of the peak assigned to Cr(VI).

The main interest was focused on the area around 900 cm^{-1}. The presence of Cr(VI) affects arising the peak at 907 cm^{-1} in the spectrum (Fig. 8). However, its intensity depends on the concentration of Cr(VI) in the sample.

The collagen hydrolysate was yellow liquid with dry mass content of 1.3 %. The measured concentration of Cr(VI) was 8.18 $mg.L^{-1}$ (method with phosphate buffer). Total concentration of chromium was for comparison 8.66 $mg.L^{-1}$ (AAS).

Fig. 9 compares Raman spectra of samples of hydrolysate (dry matter) and of ash from leather, which is containing significantly higher content of hexavalent chromium.

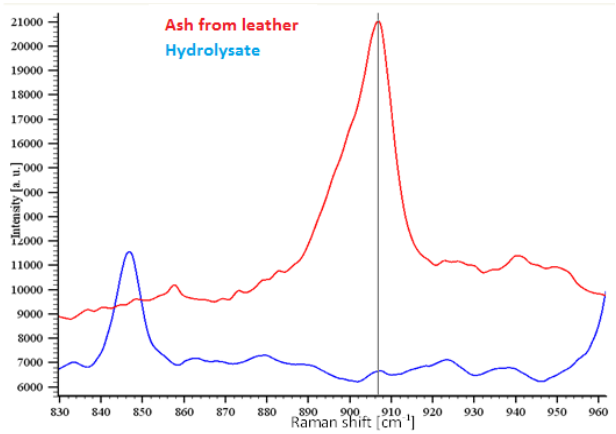

Fig. 9: Raman spectra of hydrolysate dry matter (blue) and ash from leather sample with significant content of Cr(VI).

5 Conclusion

The goal of this paper was to provide an overview of available information about spectrometric determination of Cr(VI), especially spectrophotometric methods using 1,5-diphenylcarbazide, and evaluation of comments for real samples measurement. Even in times of modern techniques, this old method is still taking its place in laboratory analyses. A big advantage is its simplicity. It has been found that this method can detect reliably the concentrations of Cr(VI) from 0.02 $mg.L^{-1}$ for given performance. Pre-treatment of the samples could play important role in final measurement and it has to be taken into account. The basic version of the method without pre-treatment steps may not be sufficient. The performance will differ according to the nature of the measured samples. Small concentrations of hexavalent chromium were found in all measured samples. The presence of Cr(VI) in the hydrolysate and in leather ash was measured using Raman spectroscopy as a fast tool of its determination. This work is a part of larger research and continues by determination possibilities of Cr(VI) in leather waste on lower level.

6 Acknowledgement

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