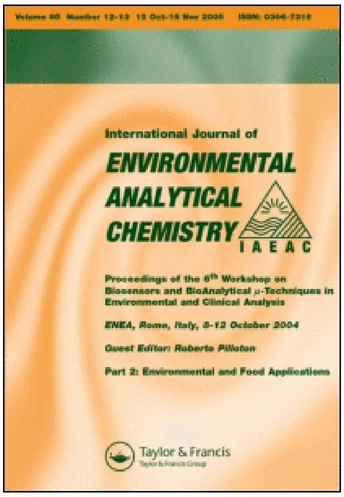

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# STUDY OF Cr(VI) IN ASHES FROM FLUIDISED BED COMBUSTION OF LEATHER WASTE: APPLICABILITY OF DIFFERENT SPECIATION METHODS

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Leather waste originated from shoe industry is considered potential hazardous waste as a consequence of the chrome tanned leather process. On the other hand, the leather waste has an inherent value as fuel that makes feasible its use as a very interesting potential source of energy; nevertheless ash residues are produced during the combustion process. This waste disposed in landfills can cause leachate problems. For that reason, determination of hexavalent chromium is considered as an essential input parameter for the safe disposal of these residues. However the current methods provide ambiguity in the results. The objective of this work was to evaluate two different speciation methods: Method SLC 22 (IUC 18) called Method I, used for leather technicians and Method II, developed by the Analytical Chemistry Laboratory of CIEMAT, to analyse the Cr(VI) content in ashes from fluidised bed combustion of leather waste. Both methods provide appropriate results for these kinds of samples when a non-reducing environment is present.

*Keywords:* Chromium (VI); Ashes; Speciation methods; Leather waste

## INTRODUCTION

Leather is a fibrous protein, a collagen cross-linked into a three-dimensional network. Raw hides are processed into usable leather through tanning to improve its appearance, physical stability and resistance to chemicals. Metal-based salts are almost universally used for tanning. The chromium compounds are preferred for most tanning operations. The metal, generally in the form of chromium trioxide ($Cr_2O_3$), roughly varies from 3 to 4% by weight in the tanned leather.

Leather waste, tannery scraps (mainly trimmings and shavings) and cutting and buffing dust, originating from shoe industry, are considered potential hazardous residues. The primarily responsible element for turning leather waste into a disposal

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problem is chromium. Cr(III) compounds have low solubility and mobility. As opposed to this, Cr(VI) compounds are classified as a human carcinogens, being rather mobile. This fact is important in terms of potential groundwater contamination. This waste, disposed in landfills, can cause leachate problems for extended periods of time since its degradation is very slow, leading to increasing stringent regulatory restrictions in the leather industry to manage the pollution source term.

On the other hand, the leather waste has inherent value as fuel. The heating value ranges from 12.5 to 21 MJ/kg, corresponding to the heating value of many brown coals. This waste is a potential source of energy. However, different contaminants (mainly hexavalent chromium) and their concentration levels should be studied not only during the combustion process but also in the final waste.

Because of the high toxicity of Cr(VI), it is very important to verify that during the combustion process the Cr(III) present in the leather waste does not alter its valence to Cr(VI). This requires reliable techniques to extract and detect, without alteration, small quantities of Cr(VI) from complex sample matrices in the presence of a large excess of Cr(III), as well as of other potential interfering compounds.

EPA [1] recognises four methods for the determination of Cr(VI): Method 7195 (Coprecipitation); Method 7196A (Colorimetric); Method 7197 (Chelation-Extraction); Method 7198 (Differential Pulse Polarography). None of them is directly applicable for this purpose as published [2], being necessary some modifications to obtain reliable results. None of them was applied directly to the analysis of ashes from fluidised bed combustion of leather waste. The problem of determination of Cr(VI) in this type of ashes is the high Cr(III) content.

Nazario and Menden [3] studied the ambiguity produced by some of these EPA methods. Their results indicate limitations in quantifying Cr(VI) in Cr(III) matrices. Coprecipitation method was shown to be unsuitable for determination of small amounts of Cr(VI) in high Cr(III) content substances. Chelation–Extraction was able to detect the presence of Cr(VI) in Cr(III) matrices, but it was unable to quantify the amount. Colorimetric analysis proved to be the most reliable, consistent and informative of all the three methods. But they worked only with spiked samples prepared in a clean water matrix, where all methods should optimally determine Cr(VI), not with real leather extracts.

In this particular instance, Method SLC 22 (IUC18) [4], called Method I in this work, was further developed specifically for the determination of Cr(VI) in leather samples, but not for this kind of ashes. As a consequence of these limitations, the Analytical Chemistry Laboratory of CIEMAT developed a new analytical method [5], called Method II, that analyses Cr(VI) in solution by colorimetry after sulphuric extraction from leather waste and its combustion ashes.

In this article, Methods I and II have been used to determine the hexavalent chromium present in different types of ashes.

## EXPERIMENTAL

### Samples

To produce energy from leather waste it is necessary to use a good combustion technology. Fluidised bed combustion is a relatively new technology in the field of waste incineration. Major advantages of this technology include relatively low and uniform furnace temperature (840–900°C) which permits the combustion to occur below the ash fusion temperature providing the optimum temperature for acid gases capture ($SO_2$ and HCl), using limestone as sorbent, and reducing $NO_x$ formation.

This technology generates ash residues with somehow different properties due to the low combustion temperature and high air velocity, which transports part of the bed material with the flue gases [6]. Several ash streams are produced during the incineration process as bottom, filter and cyclone ashes.

In order to carry out this work, several ash samples were prepared from fresh leather waste. Table I shows the immediate and ultimate analyses of this leather waste. At the same time, it is necessary to know the original chromium content of the leather waste used as fuel on the combustion tests. This is shown in Table II, as well as the major constituents of the leather ash chemical composition.

Two groups of ash samples were prepared with this leather waste. The first group was constituted by thirteen samples, obtained by combustion of fresh leather in a heating plate. The ashes were prepared at different experimental conditions, such as weight of sample, size of porcelain crucible and combustion time. The process was as following: leather was weighted in different porcelain crucibles, burnt to ashes in a heating plate and then maintained in an oven at 850°C during 1–3 h. CaO was added to four samples, in different quantity (0.5–1%) to promote the oxidation of Cr(III).

The second ash sample group (30 samples) was obtained by burning leather waste on the bubbling fluidised bed combustion pilot plant of CIEMAT. The system comprised a combustor of 30 cm inside diameter and 3.25 m height, a fuel feeding system, an air line, two cyclones, a heat exchanger, a bag filter and an on-line flue gas analyser. Figure 1 shows a schematic diagram of the experimental setup. The operating conditions in each test were as following: combustion temperature 850°C,

TABLE I Immediate and ultimate analyses of leather waste

| | |
|---|---|
| Immediate analysis (%) | |
| Volatile matter | 66.4 |
| Ash | 4.5 |
| Fixed carbon | 15.8 |
| Moisture | 13.3 |
| Ultimate analysis (% d.b.) | |
| Carbon | 54.8 |
| Sulphur | 1.4 |
| Nitrogen | 14.1 |
| Hydrogen | 5.2 |
| Oxygen | 19.3 |
| Ash | 5.2 |
| Low Heating Value (MJ/kg) | 18.1 |

TABLE II Major constituents (%) of the leather ash chemical composition

| | |
|---|---|
| $Cr_2O_3$ | 88.9 |
| $Al_2O_3$ | 2.1 |
| CaO | 7.3 |
| $Fe_2O_3$ | 1.7 |

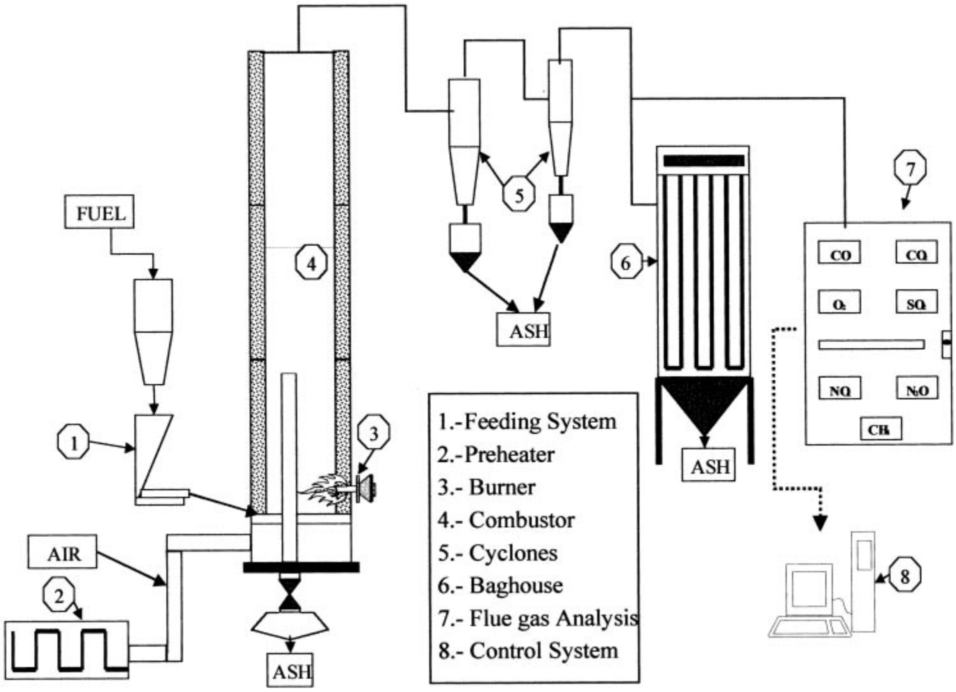

FIGURE 1 CIEMAT bubbling fluidised bed pilot plant.

fluidisation velocity 1.2 m/s and oxygen excess 5%. Only cyclone and filter ashes were collected for the analysis of Cr(VI), since they are the main source of ash residues. These ashes contain considerable amounts of soluble substances such as chromium compounds.

## Methods

The analytical characteristics of the four EPA methods for the determination of Cr(VI) mentioned in the introduction are displayed in Table III.

Hexavalent chromium present in ashes was determined by colorimetric diphenylcarbazide (DPC) analysis. Two variations on the DPC analysis were used in this work: Method I taken from International Standards (SLC 22 or IUC 18), and Method II developed in the Analytical Chemistry Laboratory of CIEMAT. Both methods use diphenylcarbazide as Cr(VI) indicator but under different and well-defined conditions:

*Method I*: 2 ± 0.01 g of ash sample were extracted by shaking, for 3 h, on a mechanical shaker with 100 mL of degassed extraction solution at pH 7.5–8.0 under inert gas. The oxygen is displaced by passing oxygen free argon or nitrogen into the flask for 5 min at 50 mL/min. After 3 h of extraction, the pH of the solution will be between 7.5 and 8.0. Otherwise the complete procedure shall be started again reducing the sample weight. Immediately after the extraction, the extract is filtered through Teflon or nylon membrane filter of 0.45 μm pore size. The extract is passed into a 100 mL volumetric flask and made up with distilled water. 10 mL of extract, or the

TABLE III Summary of EPA methods for the analysis of Cr(VI) in solid waste

| *EPA Method* | *Principle* | *Concentration range* | *Interferences* |
|---|---|---|---|
| 7195<br>Coprecipitation | Separation of Cr(VI) from solution by coprecipitation of $PbCrO_4$ with $PbSO_4$ in a solution of acetic acid. Either AAS or FAAS can be used with coprecipitation | $> 5\,\mu g/L$ | $[SO_4^{2-}, Cl^-] > 1000\,mg/L$ |
| 7196A<br>Colorimetric | Dissolved Cr(VI) in the absence of Mo, V and Hg may be determined colorimetrically by reaction with diphenylcarbazide in acid solution at 540 nm | 0.5–50 mg/L | [Mo(VI), Hg] > 200 mg/L<br>[V] > 10 [Cr(VI)]<br>[Fe] > 1 mg/L |
| 7197<br>Chelation–Extraction | Chelation of Cr(VI) with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with MIBK. The extract is aspirated into the flame of an AAS | 1–25 μg/L | High concentrations of other metals |
| 7198<br>Differential pulse polarography | It measures the peak current produced from the reduction of Cr(VI) to Cr(III) at a dropping Hg electrode during a differential pulse voltage ramp. The supporting electrolyte is $0.125\,M\ NH_4OH–0.125\,M\ NH_4Cl$ | 1–5 mg/L (depending on the Hg drop size) | [Cu] > [Cr(VI)]<br>Reducing species; $Fe^{2+}$, $SO_3^{2-}$, $S^{2-}$ |

adequate volume, depending on the Cr(VI) content, are dispensed into a 50 mL volumetric flask and diluted to 3/4 of its volume with distilled water. 1 mL of 10 g/L DPC solution is added followed by 1 mL of phosphoric acid solution. The content of the flask is mixed and made up to 50 mL with distilled water. It is allowed to stand for 15 ± 5 min and the absorbance of the solution at 540 nm measured in a 1 cm cell against the blank solution. Another aliquot of the same volume of extract is dispensed into a 50 mL volumetric flask, as before, and treated as described above, but without the addition of the DPC. The absorbance of this solution is known as colour correction and it is especially necessary for its correction in coloured extracts.

A suitable calibration curve may be plotted by using 0.25/0.5/1.0/1.5/2.0/2.5 and 3.0 mL of the 10 mg/L Cr(VI) standard solution. These volumes are dispensed into 50 mL volumetric flasks and 1 mL of 10 g/L DPC solution is added, followed by 1 mL of phosphoric acid. Next make up to volume with distilled water, mix well and allow to stand for 15 ± 5 min like samples. The Cr(VI) concentrations in mg/50 mL are plotted against the measured absorbance.

*Method II*: 25–50 ± 0.01 mg of ashes were digested, stirring and heating with 25 mL of 10% $H_2SO_4$ for 45 min. After the digestion, the extract is filtered, cooled and made up to 100 mL into a 100 mL volumetric flask with distilled water. 20 mL of the extract, or the adequate volume depending on the Cr(VI) content, is dispensed into a 50 mL volumetric flask and made up to 50 mL with distilled water. 2.5 mL of 0.4 g/L DPC solution is added. The content of the flask is mixed, allowed to stand for 15 ± 5 min and measured at 543 nm in a 1 cm cell against the blank solution.

A suitable calibration curve may be plotted by using 0.25/0.5/1.0/1.5/2.0/2.5 and 3.0 ml of the 10 mg/L Cr(VI) standard solution. These volumes are dispensed into 50 mL volumetric flasks, 1 mL of 50% $H_2SO_4$ is added and made up to volume with distilled water, mixing well. Then 2.5 mL of 0.4 g/L DPC solution are added. The content of the flask is mixed, allowed to stand for 15 ± 5 min and measured like the samples. The Cr(VI) concentrations in mg/52.5 mL are plotted against the measured absorbance.

## Regeants

All used reagents were at least of analytical-reagent grade.

### *Method I*

- 228 g/L extraction solution: 22.8 g dipotassium hydrogen phosphate $K_2HPO_4 \cdot 3H_2O$ dissolved in 100 mL water, adjusted to pH 8.0 ± 0.1 with 70% phosphoric acid.
- 10 g/L DPC solution: 1.0 g de 1.5-diphenyl-carbazide CO $(NHNHC_6H_5)_2$ dissolved in 100 mL acetone and made acidic with one drop of $CH_3COOH$. The shelf life is up to 14 days at 4°C.
- 70% phosphoric acid solution: 700 mL *o*-phosphoric acid, $d = 1.71$ g/mL, made up to 1000 mL with distilled water.
- 1 g/L chromium (VI) stock solution: 2.829 g potassium dichromate ($K_2Cr_2O_7$) dissolved in a volumetric flask and made up to 1000 mL with distilled water. (1 mL of this solution contains 1 mg of chromium.)
- 10 mg/L chromium (VI) standard solution: 1 mL of the chromium stock solution is dispensed into a 100 mL volumetric flask and made up to the mark with distilled water. (1 mL of this solution contains 1 μg of chromium.)

- Argon or nitrogen, oxygen free.
- Distilled water.
- Potassium dichromate ($K_2Cr_2O_7$) dried for 16 ± 2 h at 102 ± 2°C.

### *Method II*

- Perchloric acid: 1.67 kg/L; 70% purity.
- Sulphuric acid: 1.84 kg/l; 95–98% purity.
- 10% sulphuric acid solution: 100 mL sulphuric acid, $d = 1.71$ g/mL, made up to 1000 mL with distilled water.
- 0.4 g/L DPC solution: 0.2 g de 1.5-diphenyl-carbazide CO $(NHNHC_6H_5)_2$ dissolved in 100 mL ethyl alcohol 95% and mixed with an acidic solution of 40 mL sulphuric acid and 360 mL distilled water. The solution should be kept in a brown bottle at 4°C.
- 1 g/L Chromium (VI) stock solution: 2.829 g potassium dichromate ($K_2Cr_2O_7$) dissolved in a volumetric flask and made up to 1000 mL with distilled water. (1 mL of this solution contains 1 mg of chromium.)
- 10 mg/L Chromium (VI) standard solution: 1 mL of the chromium stock solution is dispensed into a 100 mL volumetric flask and made up to the mark with distilled water. (1 mL of this solution contains 1 μg of chromium.)
- Potassium dichromate ($K_2Cr_2O_7$) dried for 2 ± 0.1 h at 110 ± 2°C.

Two solid standards were prepared from chromic oxide ($Cr_2O_3$) and potassium dichromate ($K_2Cr_2O_7$) analytical commercial products: Standard 1 has 61.58% of Cr(III) and 3.54% of Cr(VI). Standard 2 has 67.74% of Cr(III) and 0.35% of Cr(VI). It was necessary to know the effectiveness of each method to recover Cr(VI), since certificate reference materials (CRM) were not available for this purpose. It is important to determine the recovery rate in order to provide information about possible matrix effects since it may have influence on the results.

### Apparatus

The laboratory apparatus used in this work were:

- 8000 Spex Mixer/Mill used to homogenise samples and standards.
- G-10 Gyratory shaker; New Brunswick Scientific Edison N.J. USA. 50 ± 10 $min^{-1}$.
- UV-160A UV-Vis recording spectrophotometer Shimadzu. Wavelength 540 nm. Photometric cell, quartz, 1 cm length.

## RESULTS AND DISCUSSION

Ashes from fluidised bed combustion of leather waste constitute a particular matrix with special characteristics with respect to soils or sediments [7,8]. The behaviour of Cr(Vl) in these latter matrices has been studied in a lot of research projects. However, this waste is generated by a dispersed industry, and, consequently, few efforts have been made to study the way to determine accurately and efficiently the content of Cr(VI) in these samples and to avoid the presence of this toxic species in the environment.

## Comparison of Methods

During the present work, most of EPA methods referred in Table III were tested. Since the differential pulse polarography technique was not available, Method 7198 could not be used. Water samples and real combustion ash extracts were spiked with Cr(VI). Good results were obtained for spiked water samples, but low recoveries were found with spiked ash leachates. As a consequence, the method used by leather technicians for leather samples (SLC 22 (IUC 18) or Method I) was considered for application to their combustion ashes. On the other side, the method developed by the Analytical Chemistry Laboratory of CIEMAT (Method II) to determine the Cr(VI) from leather waste and its combustion ashes was used as an alternative, drawing a comparison of the results obtained by both methods.

The main differences between Methods I and II are pointed out in Table IV. The Cr(VI) extraction procedure is completely different. While this process takes place in Method I at a pH range of 7.5–8 (controlled by $K_2HPO_4$–$H_3PO_4$ buffer), it needs strong acid medium ($H_2SO_4$) in Method II. Cr(VI) is strongly dependent on the pH [9]. Therefore Cr(VI) is easier to reduce as acidity increases. However, this reduction may be kinetically slow, and extended storage time could cause significant losses of Cr(VI). In this sense, extraction according to Method II could lead more easily to losses than Method I. On the other hand, Method II has a higher capability to solubilise different forms of Cr(VI), because of its low pH level. Consequently, the non-solubilised Cr(VI) would be undetected.

The mechanism used to detect Cr(VI) is basically similar in both methods: oxidation of added DPC to diphenylcarbazone (DPCO) by present Cr(VI) in acidic solution, followed by the formation of a soluble strongly red-violet complex with generated Cr(III) (Cr(II1)–DPCO$^{(3-n)+}$). The concentration of DPC in Method I is 10 times higher than in Method II, but the ratio between this concentration and the weight of sample in Method II is 4 to 8 times higher. In this sense, a large excess of DPC is essential since compounds that consume reagent reduce the reaction capability.

Several samples of the first group were analysed using both methods. A comparison of the results is represented in Fig. 2. A lot of points are grouped in a small area corresponding to different experiences made with the same sample treated under similar

TABLE IV Main differences between Methods I and II

| *Parameter* | *Method I* | *Method II* |
|---|---|---|
| Weight of sample | 2 g | 0.025–0.050 g |
| Extraction time | 3 h | 45 min |
| Extraction pH | 7.5–8 ($K_2HPO_4$–$H_3PO_4$ buffer) | Strong acid (10% $H_2SO_4$) |
| Extraction $T^a$ | Room temperature | Heating |
| DPC | 1 mL of 10 g/L DPC | 2.5 mLof 0.4 g/L DPC |
| DPC medium | Acetone | Ethyl alcohol–$H_2SO_4$ |
| Concentration range (μg Cr(VI)/g ash) | 5–10 | 100–200 |
| Relative standard deviation (%) | 4.8 | 7.1 |
| Detection limit (μg/L Cr(VI)) | 7.29 | 10.7 |
| Detection limit (μg Cr(VI)/g ash) | 1.82 | 71.4 |

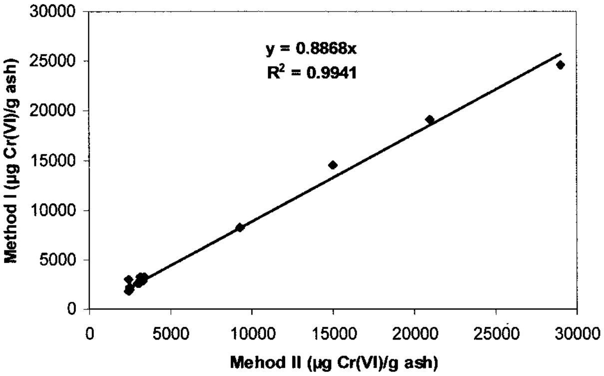

FIGURE 2 Correlation of the results obtained by Methods I and II.

experimental conditions. The rest of the points represents results of samples treated with CaO, compound intentionally added in order to induce the formation of Cr(VI). The correlation between both methods is quite acceptable ($R^2 = 0.9941$). However, the results obtained by Method I are significantly lower than those found by Method II (slope 0.8868 in Fig. 2). This fact could be explained by several reasons. One of them is the weight of sample; that is much higher in Method I than in II. As weight increases, the interaction with the reagent is getting worse and the efficiency in the extraction of Cr(VI) decreases. Other reasons are the leaching temperature and pH. The heating provides a better extraction. A low pH facilitates the oxidation of DPC by chromate and increases the dissolution process of a lot of concomitants, releasing the Cr(VI) bound to them.

The reducing compounds from certain samples may compete with DPC to react with Cr(VI) to produce undetected products. In these cases, although an increase of DPC concentrations could be necessary in order to complete the formation of red-violet coloured complex, it has been tested in both methods that it does not cause an increase on the signal.

The detection limits of both methods were estimated as three times the standard deviation of 20 measurements of solutions previously reduced to Cr(III) to avoid the presence of Cr(VI). Their values are in Table IV, referred to the solution and to the solid sample.

Method I has better sensitivity and precision, but it is more time-consuming. This method is a useful way for determination of Cr(VI) in samples with low levels of this analyte and with a low degree of homogeneity. The amount of sample used in the analysis is up to 2 g, a more representative fraction of the whole sample than smaller sample weights.

## Recovery of Spiked Cr(VI)

This test was carried out to evaluate the recovery of Cr(VI) spiked in several steps throughout the process. The recoveries of the concentration of added Cr(VI) have particular importance because there are no standard reference materials for Cr(VI) analysis in samples of leather combustion ashes. Different additions of a synthetically solution of Cr(VI), or Spike 3, to the measurement solution were made to study the detection and quantification process. Several fractions of a solid standard with a high concentration of $Cr_2O_3$ and important amounts of $K_2Cr_2O_7$ were also added to the solid ashes in order to evaluate the extraction and measurement processes. Figure 3 shows a scheme of the places and types of spiking. Spike 3 was used to evaluate the responses of the instrumental methods in such leachates. This evaluation is wider for Spike 2, since it considers also the extraction process. The recoveries of Spike 1 also include both the dissolution process of Cr(VI) and the presence of a high concentration level of Cr(III).

The results of the recoveries obtained with two different levels of concentration (**H** = high level, 500 μg/g and **L** = low level, 80 μg/g) are represented in Fig. 4 for every spike and method. The corresponding amount of Cr(VI) leached from original ashes has been subtracted. Each error bar was estimated from the standard deviation of at least five spiked samples. The Spike 3, addition of a solution of Cr(VI) before the instrument analysis, shows the best recoveries, ranging from 96 to 102%, with a standard deviation lower than 5% for five measurements.

When the additions were made before the extraction procedure, the precision of the results was worse, since the samples and the additions were subject to the extraction and determination process. In these cases, slight differences in the obtained recoveries were found when a solution of Cr(VI) (Spike 2) and a solid mixture of high concentration of $Cr_2O_3$ and low level of Cr(VI) (Spike 1) were employed.

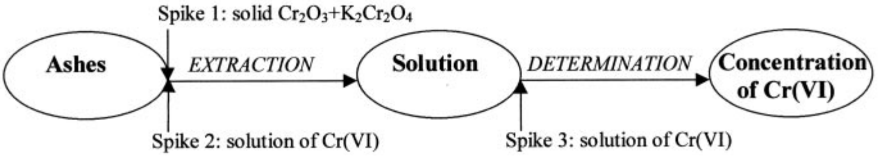

FIGURE 3 Scheme of the places and types of spiking.

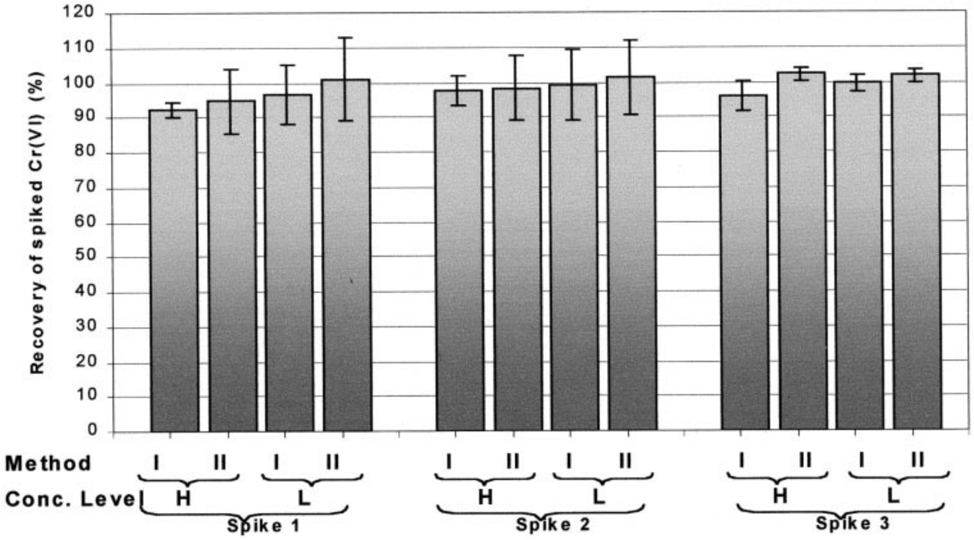

FIGURE 4 Recoveries obtained with two different levels of concentration for every spike and method of analysis.

Similar precision and lightly lower recoveries are obtained in the Spike 1. That means that the presence of an excess of Cr(III) does not imply an increase in the signal, as a consequence of an induced oxidation of Cr(III) to Cr(VI), although the opposite effect is weakly produced (an induced reduction of Cr(VI) to Cr(III)). On the other hand, this effect is shown mainly for high concentration of Cr(VI), where the recoveries are lower than those expected, being the standard deviation of the results higher for the low concentration level.

## Matrix Effects

A similar experience was carried out with cyclone and filter ashes coming from combustion of fresh leather waste on the fluidised bed combustion pilot plant of CIEMAT. The behaviour of most of these samples was similar to that of previous experience and the same degree of recovery was obtained for the Spikes 1–3. However, other specific samples showed an anomalous behaviour: recoveries of the Spikes 1–3 were even lower than 10% for Method I. Method II was less prone to these alterations. The results for the Spike 3 were acceptable, but not for the Spikes 1 and 2, where the signals are highly dependent on the volume of sample taken for analysis.

This unusual behaviour could be attributed to various reasons:

1. An incomplete dissolution of added solid Cr(VI).
2. An insufficient concentration of free DPC to complete the reduction of Cr(VI) and the quantitative formation of the complex (Cr(III)–DPCO$^{(3-n)+}$).
3. A reducing capability of the ashes. The presence of certain compounds inherent to the sample could reduce Cr(VI) to Cr(III) without the addition of reagent.

The incomplete dissolution of the added solid Cr(VI) would lead to low recoveries for Spike 1, but close to 100% for Spikes 2 and 3. In these ashes the recoveries are very low for the three spikes. Both phosphate buffer and sulphuric acid extract essentially non-measurable Cr(VI) from the Spike 1, what may indicate that the Cr(VI) was solubilised and then reduced to Cr(III) by other reducing compounds present in the solution. The hypothesis on that Cr(VI) is not solubilised in these media, and therefore, is not recovered, is refused, because the results of an equivalent experience without real samples showed a complete recovery of the added Cr(VI).

On the other hand, it could be assumed that the concentration of DPC is not high enough to reduce Cr(Vl) in presence of interfering components, such as strong oxidising agents, that may compete with Cr(VI) to oxidise DPC. Consequently, a new test was made based on the addition of an extra amount of DPC to the extracts. The results obtained in this way were similar to those corresponding to lower concentration of DPC. When the addition of DPC was made at the beginning of the extraction process, a red-violet colour was only observed in Method II at 15 min. This colour was decreasing with time and disappeared at the end of the extraction. With new additions of DPC the colour was not recovered. These facts corroborate that the reason for the low recoveries of added Cr(VI) is not the lack of enough amount of DPC.

It was considered more plausible that reduction of dissolved Cr(VI) by some other ash components took place. The quantification of Cr(VI) in ash extracts demonstrates that when the samples contain strongly reducing matrix components and/or the concentration of Cr(VI) in the sample is low, both methods may not become suitable for Cr(VI). In these types of samples both methods can not be applied. However, in these conditions Cr(VI) is not stable and it can not be present as a contaminant. As a consequence, it is necessary to know whether each sample has a reducing or non-reducing character.

## Conditions for the Suitable Application of the Methods

Two different procedures have been developed in order to establish the limit conditions for application of the methods; one of them is based on the measurement of redox potential at the end of the leaching process, and the other on the comparison between slopes obtained by both standard addition method and direct analysis of the final extract. Both methods provide consistent results, but from a practical point of view, the former is more useful and less time-consuming.

### *(i)Procedure Based on the Measurement of Potential*

Values of pH and redox potential were registered at the beginning and at the end of the extraction process for several normal and anomalous samples. While the redox potential values were found to be in a wide range, the pH values ranged between 7.5 and 8 as expected for Method I and showed a strongly acidity for Method II. Solutions from Method I showed unstable potential measurements. The values were ranged between 140 and 250 mV, and a weak evolution was observed within the extraction time.

Values ranging between 330 and 670 mV were measured with Method II, and an evident reduction of the potential can be found along the extraction process. In both methods a remarkable difference in the redox potential of the extracts can be seen, showing an anomalous behaviour in relation to the others. Therefore, a limit of application for each method can be established as a function of this parameter measured at the end of the leaching process. Ashes with an unusual behaviour are those with a potential lower than 200 mV for Method I and 600 mV for Method II. Since these limit values should be modified as a function of the concentration of Cr, it is recommended to deduce the recovery for a single spike for each sample. The application of the methods will be suitable only when the deduced recoveries are in the 90–110% range. Low recoveries for spiked Cr(VI) may be an indicator of the tendency for generated Cr(VI) to persist under field conditions over long term in a non-reducing context. In these samples with a reducing matrix, the detection limits could be higher because the matrix may compete with DPC to react with Cr(VI) to produce undetectable products.

### *(ii) Procedure Based on the Comparison Between Slopes*

Another way to check the absence of matrix effects is the comparison of the slopes obtained by the standard addition method and direct analysis. Differences higher than 10% show the disability of the method to provide suitable results. A minimum difference between both slopes is an indicator of the absence of such effects. The slopes deduced for samples with anomalous behaviour are quite different, and in some cases it is even impossible to determine Cr(VI) with the standard addition method since the added Cr(VI) does not increase the absorbance.

## Influence of the Ash Treatment

The use of the bubbling fluidised bed technique for treatment of the leather waste is rather a new concept for the controlled disposal of these residues. This type of combustion produces ash residues with different characteristics than the ashes generated in a laboratory scale mass burn. For instance, the combustion temperature is more homogeneous in an industrial than in a laboratory scale process, since the burning of the waste is made in a continuous form. On the other hand, the process in a laboratory takes place with a very low amount of sample and in presence of an oxygen environment. This means that the components of the ashes could be in different oxidation states according to the combustion process, and the oxidation of Cr(III) is more feasible in the laboratory scale assays.

The results for the studied samples showed a higher precision in the fluidised bed combustion ashes. The main source of variability in the results for the samples prepared in the laboratory was the combustion process. The differences were higher than those corresponding to replicated analyses and even to the use of different analytical methods. Ashes prepared with combustion times of 1 or 3 h provide similar results. Remarked differences were found with samples burnt in different size crucibles, and the amount of initial leather waste was also relevant.

## Influence of the Presence of CaO on the Combustion Process

Limestone ($CaCO_3$) is a sorbent frequently used in fluidised bed combustion to remove the acid gases (mainly $SO_2$) present in the flue gases. The overall reaction for the sulphation takes place by the decomposition of $CaCO_3$ to CaO during the calcination process produced in the bed, at the same time as the combustion process. To obtain high sulphur retention it is necessary to use a Ca/S ratio higher than 2. So CaO excess is a characteristic of that combustion process where limestone is added.

Several tests were made in the laboratory, using CaO in the combustion step. Concentrations of this compound ranging between 0.5 and 1% were used. The obtained results show a progressive increase in concentrations of Cr(VI) as a function of the added CaO, independently of the method used for the determination. Other experiences in combustion pilot plant have shown the same tendency [10].

Consequently it can be deduced that CaO induces the oxidation of Cr(III) to Cr(VI) in the combustion process. This conclusion agrees with the obtained by other researchers [10]. This is one of the main reasons for avoiding its use in the experiments carried out in the CIEMAT pilot plant.

Although the leather ashes have a high content of this compound (7.3% of Ca expressed as CaO), the addition of this compound in the fluidised bed is not recommended for these raw materials with a high level of Cr(III).

## CONCLUSIONS

Method SLC 22 (IUC18) used by leather technicians for determination of Cr(VI) in this material is applied to their ashes with good results. Another method, developed in the Analytical Chemistry Laboratory of CIEMAT, is employed as an alternative. Both methods are compared, providing appropriate results for this determination in ashes from fluidised bed combustion of leather waste when a non-reducing environment is present.

The former method is more sensitive and precise and is more independent of the homogeneity of the sample. The latter is easier and less time-consuming. Three types of Cr(VI) spiking have been tested to evaluate the complete analytical process, including dissolution, extraction and instrumental measurement. Recoveries of the spikes agree with the expected values for two levels of concentration and for both methods.

In some cases, ashes coming from fluidised bed combustion show an anomalous behaviour, with low recoveries of spikes. It could be attributed to the reduction of present or added Cr(VI) to Cr(III) by the reducing compounds inherent to the ashes. In these situations none of the methods can be applied, but the intrinsic characteristics of the samples avoid the generation and permanence of Cr(VI). Therefore, the limit parameters for the application of the studied methods are established by two different procedures based on the measurement of the redox potential of the extract and on the comparison of the slopes corresponding to the standard addition and direct analysis methods.

In general, ashes generated in a fluidised bed combustion process had a higher degree of homogeneity and lower concentrations of Cr(VI) than those prepared in the laboratory. In the latter, the crucible size and the amount of initial leather waste were the main sources of variability in the results. The laboratory tests proved that CaO induces the oxidation of Cr(III) to Cr(VI).

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## *References*

[1] Test Method for Evaluating Solid Waste, Physical/Chemical Methods, SW 846, 3rd Edn., November 1986, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.
[2] F. Rutland, W. Kallenberger, E. Menden and C. Nazario, *JALCA*, **85**, 326–333 (1990).
[3] C.L. Nazario and E.E. Menden, *JALCA*, **85**, 212–224 (1990).
[4] SLC 22 (IUC 18), *JSLCT*, **81**, 109–114 (1997).
[5] M.L. Munuera, M.A. Claver, J. Marín and R. Martin, CIEMAT Report Ref. QAA, 1313–1314 (1994).
[6] J. Blondin, A.P. Iribarne, E.J. Anthony, *Proceedings of 14th Fluidized Bed Combustion Conference*, ASME (1997).
[7] L.A. Heringer-Donnez and W.E. Kallenberger, *JALCA*, **84**, 110–121 (1989).
[8] A. Sahuquillo, J.F. López-Sánchez, R. Rubio, G. Rauret and V. Hatje, *Fresenius J. Anal. Chem.*, **351**, 197–203 (1995).
[9] N.K. Djiane, K. Ndung'u, C. Johnsson, H. Sartz, T. Tornstrom and L. Mathiasson, *Talanta*, **48**, 1121–1132 (1999).
[10] B.H. Jones, *JALCA*, **74**, 395–403 (1979).