

Accelerated and Automated Extraction of Hexavalent Chromium from Solid Waste Materials Coupled with Ion Chromatography Determination

C. Giuriati,^a F. Abballe,^b M.C. Cristofori^a and A. Gorni,^a

^aAmbiente SpA, Ferrara, Italy,

^bLaboratory of Application, Dionex SRL, Rome, Italy.

A new method concerning the determination of hexavalent chromium in wastes was automated, optimized and validated. The method is based on the accelerated and automated extraction of solid samples followed by ion chromatography analysis using spectrophotometric detection. Some modifications regarding the sample extraction, described in method EPA 3060A (alkaline digestion for hexavalent chromium), and some other adjustments in application of the method EPA 7199 (determination of hexavalent chromium in drinking water, groundwater and industrial wastewater effluents by ion chromatography), were performed in order to improve the reproducibility, accuracy and sensitivity of this proposed method. All tests were performed extracting spiked matrices and comparing the measurements with the results obtained in application of sample preparation method EPA 3060A; the experiments were performed on different samples of sludge and soil. The proposed method shows better reproducibility and accuracy and a significant time reduction for the analysis.

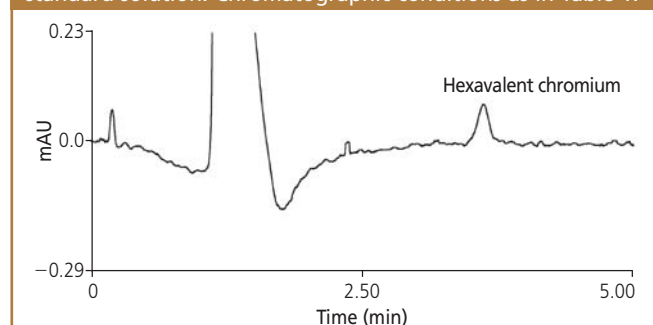
Introduction

The identification and quantification of hexavalent chromium in solid samples is an important factor in characterization studies. The speciation of elements is a developing feature of analytical methods; the evaluation of the environmental and biological impact of the Cr (VI) compounds on environmental matrices is fundamental because of their demonstrated toxicity and potential carcinogenicity on humans.^{1,2} The regulatory agencies in Italy have established restrictive limits of concentration on soil samples from reclamation areas.³ The concentration limit depends on the final destination (use) of the reclaimed soil, a maximum of 2 mg/Kg (dry matter) for residential areas and a maximum of 15 mg/Kg (dry matter) for industrial areas.

The hexavalent chromium extraction and analysis are reported in several official methods using different analytical techniques; based on spectrophotometric electrochemical methods, determination or based on atomic absorption spectrophotometry and plasma mass spectrometry.^{4,5,6} Among the valence specific direct measurements, we investigated the ion chromatography analysis coupled with spectrophotometric detection^{7,8,9,10} as described in EPA method 7199¹¹ and modified¹² in order to reach lower detection limits. (The proposed method allows a detection limit of 0.01 µg/L of hexavalent chromium and 0.1 µg/L of quantification limit as

can be seen from Figure 1).¹³ Chromatographic and detection conditions are given in Table 1. In the set up of the proposed protocol, we focused our efforts on the extraction procedure of hexavalent chromium from solid samples; well aware that the accuracy of the methods on chromium speciation in these kind of matrices needs various improvements, as is shown in a review by Marques et al.¹⁴ The lack of reported recovery by most authors emphasizes this fact. As reported in several methods, in order to quantify Cr (VI) in solid samples, three criteria have to be satisfied: the extraction solution must dissolve all forms of

Figure 1: Chromatogram of an injection of 0.01 µg/L standard solution. Chromatographic conditions as in Table 1.



Cr (VI), the extraction conditions must not cause any reduction of native Cr (VI) to Cr (III) and finally the method shall not cause oxidation of native Cr (III) contained in the sample to Cr (VI). In the EPA extraction method 3060A these three criteria are satisfied; under alkaline conditions (pH > 11.5) for the extraction with the heated carbonate-hydroxide solution, minimal reduction of Cr (VI) or oxidation of Cr (III) occurs.¹⁵ The following pH adjustment of the sample to pH 9, using nitric acid 5M, is required to allow the IC analysis with EPA 7199. Because of the lack of availability of certified matrices for the extraction validation procedures, spiked samples of soils and sludge were used. In order to reduce the manipulation of the matrices and extracts we set up an automated approach to the extraction procedure, the advantage of the automated extraction was to reduce the analysis time and possible contamination of the sample. A low variability of the Cr (VI) recovery was also noted.

Further cross references were obtained analysing solid samples previously quantified by two different laboratories in application of different valence specific-direct measurements. The method optimization is at present still in progress.

Experimental

Reagents, standards and materials: All chemicals used in this work were of analytical grade, the details can be found in protocols EPA 3060A and EPA 7199. Potassium dichromate as an alternative to certified primary standard solution can be used, ammonia solution 30%V/V, ammonia sulphate, 1,5 diphenylcarbazide, methanol (HPLC grade), concentrated sulphuric acid, dipotassium, hydrogen-phosphate and potassium dihydrogen-phosphate, (Carlo Erba, Milan, Italy).

Hydromatrix®: Varian

Isolute® sorbent: International Sorbent Technology Ltd (Hengoed, Mid Glamorgan, UK).

Sand: J.T. Baker (Deventer, The Netherlands).
 Quartz grains: 1–2 mm Baker grade J.T. Baker, Deventer, The Netherlands.
 Disposable syringe
 filter device: Nylon filter media with polypropylene housing, 0.45 µm pore size Whatman and filter papers 41 ashless circles, 110 mm Dia Whatman (Maidstone, England).

Instrumentation and analytical set-up: Chromatographic analysis was performed using an ion chromatograph model DX600 (Dionex Corp., California, USA), with the following configuration: gradient pump GP50, AS50 autosampler,

The evaluation of the environmental and biological impact of the Cr (VI) compounds on environmental matrices is fundamental because of their demonstrated toxicity and potential carcinogenicity on humans.

spectrophotometric detector AD25, PC10 post-column pneumatic delivery package. The 250 × 4 mm i.d. Ion Pac AS7 (Dionex Corp., California, USA) analytical column was used for the separation of hexavalent chromium. The 50 × 4 mm i.d. Ion Pac NG1 (Dionex Corp., California, USA) guard column was placed before the separation column and contained a sorbent capable of removing strongly absorbing organics that would otherwise damage the separator column. The analytical conditions described in the method EPA 7199 were modified using a larger volume reaction coil (750 µL); lower eluent flow-rate and increased injection volume. This allowed lower detection limits to be achieved. Accelerated Solvent Extractor

model ASE (Dionex Corp., California, USA) was used to extract hexavalent chromium. For each sample add 0.5 mL of 1.0 M phosphate buffer (0.5 M K_2HPO_4 / 0.5 M KH_2PO_4). The extraction conditions are summarized in Table 2.

Results and Discussion

Preliminary considerations regarding the extraction procedure:

The accelerated solvent extractor ASE uses increased temperature and pressure to accelerate extraction of solid matrices while minimizing solvent use. The accelerated solvent extraction is a method recently accepted by the US Environmental Protection Agency (EPA) for the extraction of organic compounds, such as semi-volatiles, total petroleum hydrocarbons, organochlorine pesticides, polychlorinated biphenyls, dioxins and furans, organophosphorous pesticides and chlorinated herbicides from solid matrices. It is a fully automated system that requires smaller quantities of solvent than traditional methods; because these extractions are

performed at pressures greater than 1000 psi, solvents can be heated to temperatures in excess of their normal boiling point. This results in a much more efficient extraction process.¹⁶

ASE meets requirements for extraction under US EPA SW-846 Method 3545A. A certain quantity of sample, 1–3 g is mixed with a dispersing inert agent, placed in the extraction tube, and heat extracted. The resulting extract is transferred to a 60 mL vial for subsequent analysis. Our first concern was to verify possible hexavalent chromium release from the ASE extraction stainless steel vessels and tubes. Using the sample extraction conditions we performed the extraction cycles on an empty cell.

The hexavalent chromium system blank was negligible. The pH adjustment with sodium hydroxide (pH >11.5) recommended in the sample preparation protocol of EPA 3060A is not suitable for the ASE system.¹⁷ In order to avoid possible damage to the ASE instrumentation an ammonium sulphate buffer solution was used to adjust the pH of the extraction solution to between a range value of 9–9.5.¹² Further checks regarding possible hexavalent chromium release were performed on the “filling” material, which is used as a dispersing and supporting agent. These materials are added to either facilitate the extraction process or support semi-solid samples such as sludges. Different “filling” materials such as quartz, sand, diatomaceous earth and paper were tested.

Among these tested filling materials the suitable choice, in terms of costs and blank level, was the Whatman no. 41 filter paper. The results are reported in Table 3. Another test was performed on the filling material in order to show possible capture of the hexavalent chromium. The recovery performance from the filling materials was performed spiking the different

Table 1: Chromatographic and detection conditions.

Chromatographic conditions

Column	250 mm × 4 mm IonPac AS7
Guard column	50 mm × 4 mm IonPac NG1
Eluent	250 mM ammonium sulphate 100 mM ammonium hydroxide
Eluent flow-rate	1.0 mL/min
Post-column reagent	2.0 mM diphenylcarbazide 10% methanol 1 N sulphuric acid
Post-column flow-rate	0.5 mL/min
Detection	Visible, 530 nm
Injection volume	500 µL

Table 2: Accelerated solvent extraction conditions.

ASE conditions

Oven temperature	200 °C
Pressure	1500 psi
Oven heat-up time	9 min
Static time	7 min
Flush volume	60%
Purge time	90 s
Solvents	water pH 9.0–9.5
Static cycles	4

Table 3. Hexavalent chromium release by “filling” inert material.

Filling inert materials	Hexavalent chromium (mg/Kg)
Diatomaceous earth	8
Sand	0.0190
Quarz	0.0179
Whatman n° 41	0.0348

Table 4: Recovery yield in digestion solution and filling inert material in the optimized conditions, using EPA 3060A and ASE methods.

EPA 3060A	pH >11.5	Recovery (%)	RSD (%)
Digestion solution + spike std (1 mg)	1.07 (n = 2)	107	4.3
ASE	pH 9.0–9.5	Recovery (%)	RSD (%)
Quartz sand + spike std (1 mg)	0.97 (n = 6)	98	5.22
Sand + spike std (1 mg)	0.91 (n = 6)	91	7.71
Whatman n° 41 + spike std (10 mg)	9.01 (n = 4)	90	8.94

Table 4.1: Recovery yield for EPA 3060A method using the pH conditions of ASE method.

EPA 3060A	pH 9.0–9.5	Recovery (%)	RSD (%)
Whatman n° 41 + spike std (10 mg)	8.80 (n = 6)	88	6.27
Digestion solution + spike std (1 mg)	0.76 (n = 6)	76	7.57

Table 5: Recovery, accuracy yield for hexavalent chromium in a sample of soil using EPA 3060A method and ASE method.

EPA 3060A	pH >11.5	Recovery (%)		RSD (%)	pH 9.0–9.5	Recovery (%)		RSD (%)
Soil + spike std (1 mg)	1.04 (n = 6)	104	0.43		0.76 (n = 6)	76	7.57	
Soil + spike std (10 mg)	7.74 (n = 5)	77	26.18		7.98 (n = 6)	80	0.42	
ASE				Recovery (%)				RSD (%)
Quarzsand + soil + spike std (1 mg)		0.89 (n = 7)	90		23.06			
Sand + soil + spike std (1 mg)		0.86 (n = 4)	86		20.09			
Sand + soil + spike std (10 mg)		10.59 (n = 4)	106		15.80			
Whatman n° 41+ soil + spike std (1 mg)		0.94 (n = 3)	94		5.69			
Whatman n° 41 + soil + spike std (5 mg)		4.58 (n = 6)	92		5.24			
Whatman n° 41+ soil + spike std (10 mg)		8.65 (n = 8)	87		7.96			

materials with known quantities of hexavalent chromium and using two different extraction procedures with ASE and EPA 3060A method. The results are reported in Table 4. Table 4.1 shows the spike tests for EPA 3060A method using the pH conditions of the ASE method. The next step in the optimization of the extraction procedure was the choice of two solid samples to be used as reference matrices. The lack of availability of certified matrices determined the choice of solid environmental samples previously tested to detect possible levels of Cr (VI). A stream sediment and an industrial soil were used as spiked matrices. Then different quantities of hexavalent chromium were added in order to estimate the method accuracy. This was expressed as a percentage recovery relative to the true spiked value and the efficiency of the extraction procedure. The results are reported in Table 5 for the soil sample and Table 6 for the sludge sample.

Sample Preparation

A solid sample is weighed on a paper filter (approx. 1–2 g), sealed and inserted in the ASE cell. As stated in the EPA 3060A protocol, a precise quantity (0.5 mL) of 1.0 M phosphate buffer is spiked into the cell. The extraction conditions are described in Table 2.

Prior to the IC analysis the extract is quantitatively transferred in to a 100 mL volumetric flask (if any opalescence is evident in the extract, a filtration on 0.45 µm disposable syringe filter is suggested).

Application to Real Matrices

In order to demonstrate the validity and efficiency of this automated extraction protocol, and because of the lack of certified matrices containing Cr (VI), a further approach was chosen to have comparison data between the two extraction methods. Two different laboratories were involved in the analysis of selected environmental matrices; both laboratories were using different protocols for the sample preparation and the quantification of Cr (VI). Laboratory “A” has applied the EPA 3060A for the extraction and the analysis was performed with an IC chromatograph as indicated in EPA 7199 method. Laboratory “B” has applied the IRSA 16 Q.64 vol. 3 method, Italian national protocol, whereby the Cr (VI) in the solid sample is dissolved in an acid water solution; the coloured

organic complex of Cr (VI) obtained using diphenyl-carbazide is quantified at the wavelength of 540 nm with a spectrophotometer.

Table 7 shows the data acquired by the different laboratories. As is shown at this simple stage of evaluation, there is a good similarity in the data produced on the real matrices. Further investigations and appropriate trials have to be performed to validate the extraction protocol with ASE.

Table 6: Recovery, accuracy yield for hexavalent chromium in a sample of sludge using EPA 3060A method and ASE method in sludge.

EPA 3060A	pH >11.5	Recovery (%)		RSD (%)
Sludge + spike std (1 mg)	0.75 (n = 6)	75		17.57
Sludge + spike std (5 mg)	3.09 (n = 6)	62		22.49
Sludge + spike std (10 mg)	4.05 (n = 6)	40		32.75
ASE				
				Recovery (%)
				RSD (%)
Whatman n° 41 + sludge + spike std (1 mg)	0.75 (n = 4)	75		3.09
Whatman n° 41 + sludge + spike std (5 mg)	4.04 (n = 6)	81		13.75
Whatman n° 41 + sludge + spike std (10 mg)	8.01 (n = 4)	80		5.25

Table 7: Data acquired by different laboratories.

Sample	Our Lab (ASE-IC)	Lab A (EPA3060 A-EPA7199)	Lab B (Colorimetric Method)
1	5 mg/Kg	7 mg/Kg	8 mg/Kg
2	70 mg/Kg	67 mg/Kg	90 mg/Kg
3	235 mg/Kg	177 mg/Kg	200 mg/kg

Conclusions

The alkaline extraction procedure, USEPA SW-846 Method 3060A for the preparation of soil samples is a widely used procedure in the determination of total Cr (VI). It is well known that the Cr oxidation state is matrix dependent and may be unstable once it is dissolved in either acid or basic aqueous extraction medium.

To quantify total hexavalent chromium, three criteria must be satisfied

- the extraction solution must solubilize all forms of Cr (VI)
- the conditions of the extraction must not induce the reduction of native Cr (VI) to Cr (III)
- the method must not cause oxidation of native Cr III contained in the sample to Cr (VI).

In the alkaline extraction, the solid sample is digested using a mixed solution at pH > 11.5, consisting of a solution of Na₂CO₃ and NaOH and heating between a range of 90/95° for 60 minutes. This is done to dissolve the Cr (VI). The preparation steps are extremely labour-intensive with the possibility of errors and exposition to toxic substances.

The aim of this work was to set up an automated extraction method as an alternative to protocol EPA 3060A for the preparation and analysis of hexavalent chromium Cr(VI) from soluble, adsorbent and precipitated forms of chromium compounds in soil, sludge, sediment, waste and similar solid materials.

Various tests were performed in order to optimize the different operating parameters, such as temperature, pressure, number of extraction cycles, extraction times etc. The evaluation of the quality control (QC) followed EPA 3060A method QC criteria. The preparation of blanks was performed with each digestion batch. If the detected concentration of Cr(VI) was higher than the method detection limit the entire batch had to be re-extracted.

Laboratory Control Samples (LCS) were analysed as an additional determination of method performance. Selected solid matrices spiked with an appropriate chromium compound were analysed to evaluate the recovery range of 80–120%. Spiked samples were analysed on a routine basis to estimate the method accuracy on the sample batch expressed as a percentage recovery relative to the true spiked value.

This proposed alternative operating procedure to the USEPA SW-846 Method 3060A needs further developments in order to assess, improve and maintain adequate quality of the data produced.

Acknowledgments

The authors wish to thank Kevin Hoyes for his kindness in the fulfilment of this work.

We also acknowledge the analytical support of Marco Malisardi of Centro Ricerche e Protezione Ambiente — Ambiente SpA.

References

1. US EPA Toxicological review of Hexavalent Chromium. In Support of Summary Information on the Integrated Risk Information System (IRIS). August 1998.
2. EPA- Air Toxics Website – Chromium Compound.
3. Italy. Decreto Ministeriale 25 ottobre 1999, n.471. Regolamento recante criteri, procedure e modalità per la messa in sicurezza, la bonifica e il ripristino ambientale dei siti inquinati, ai sensi dell'articolo 17 del decreto legislativo 5 febbraio 1997, n. 22, e successive modificazioni e integrazioni. G.U. n. 293 del 15 dicembre 1999.
4. Final Draft prCEN/TR 14589:2002. Characterization of waste - State of the art document – Chromium VI specification in solid matrixe.
5. Hakan Gürleyük. Fresenius –http://www.frontiergeosciences.com/frontierweb/One%20pages/Cr.html
6. CEN TC 292 WI 292037 2004–06: Characterisation of waste and soil- Determination of hexavalent chromium in soil material by alkaline digestion and ion chromatography with spectrophotometric detection- Complementary element.
7. Dionex Technical Note 26: Determination of Cr(VI) in water, wastewater, and solid waste extract.
8. Dionex Application Note 80: Determination of dissolved hexavalent chromium in drinking water, groundwater, and industrial wastewater effluents by ion chromatography.
9. EPA Method 218.6: Determination of dissolved hexavalent chromium in drinking water, groundwater and industrial wastewater effluents by ion chromatography. US Environmental Protection Agency, Cincinnati, Ohio, USA, 1991.
10. ASTM D5257-97: Standard test method for dissolved hexavalent chromium in water by ion chromatography.
11. US EPA Method 7199: Determination of hexavalent chromium in drinking water, groundwater and industrial wastewater effluents by ion chromatography. Revision 0, December 1996.
12. D.H. Tomas et al., *J. of Chromatogr. A*, **956**, 255–259 (2002).
13. A. Hubaux and G. Vos, *Anal. Chem.*, **42**, 849 (1970).
14. M.J. Marques et al., *J. Anal. Chem.*, **362**, 239 (1998).
15. US EPA Method 3060A: Alkaline digestion for hexavalent chromium. Revision 1, December 1996.
16. EPA Method 3545 A : Pressurized fluid extraction (PFE). Revision 1 A, February 2000.
17. Accelerated Solvent Extractor Operator's Manual Dionex.

Caterina Giuriati is Senior Analyst at Ambiente SpA laboratories. She works on environmental matrices such as soil, surface and underground water, stack emissions, and waste using an IC technique. She collaborates with official bureaus in the set-up and development of new methods with ion chromatography.

Franco Abballe is Support Manager for Dionex, Italy and develops analytical methods with HPLC, IC, ASE extraction and μ HPLC techniques. He also organizes training courses.

Maria Cristina Cristofori is Head of the Analytical Division at Ambiente SpA's Ferrara laboratory. She is the representative in various national and European commissions for the development of analytical methods on environmental matters.

Alfredo Gorni is Managing Director of Ambiente SpA laboratories. Ambiente is an Eni group company that works in industrial waste treatment and environmental remediation. Ferrara lab specializes in micro-pollutants (PCDD/PCDF), in conformance with EPA and EC protocols. Gorni is a biologist and expert mass spectrometrists.

