



## **Determination of Cr(VI) in Environmental Samples Evaluating Cr(VI) Impact in a Contaminated Area**

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**Abstract:** Spectrophotometric determination of  $\text{Cr}^{+6}$  (using 1.5–diphenyl carbazide), in aqueous, sediment and soil samples is reported. Different leaching reagents like 0.5M NaOH-0.28M  $\text{Na}_2\text{CO}_3$  and 0.2 M  $\text{H}_3\text{PO}_4$  were used for the isolation of  $\text{Cr}^{+6}$  from sediment and soil samples. Determination of  $\text{Cr}^6$  by using 0.5M NaOH-0.28M  $\text{Na}_2\text{CO}_3$  as leaching reagent followed by spectrophotometric measurements provided satisfied results. The optimum experimental parameters of the reactions have been studied and the validity of the described procedures was assessed. Statistical analysis of the results has been carried out revealing high accuracy and good precision. Total Cr concentration was analyzed by AASF technique. This paper explores the development and application of  $\text{Cr}^6$  chemical speciation in a polluted area and marine environment. The polluted site of Porto Romano, Durrës, pointed as “Hot Spot Pollution” from UNEP/MAP (1992) was under investigation. The content of  $\text{Cr}^{+6}$  in soil and surface water samples inside territory of polluted site is very high (some g/kg in soil samples and arrived up to 130 mg/l in surface water samples). More than 90% of  $\text{Cr}_{\text{tot}}$  belongs to its easy soluble form and only 2–10% of it belongs to the form bounded with soils. The content of  $\text{Cr}^{+6}$  in seawater (about 0.04 mg/l) and sediment (5-6 mg/kg as  $\text{Cr}_{\text{tot}}$ ) samples resulted within the normal levels. Only 11 to 13% of  $\text{Cr}_{\text{tot}}$  belongs to its easy soluble form and most of it (87–89%) belongs to the form bounded with sediments.

**Keywords:** chromium, speciation, water, sediments and soils, UV-Vis spectrophotometry, AAS.

### **Introduction:**

Chromium is a naturally occurring element present in water, sediments, rocks, soils, plants, biota, animals, and volcanic emissions. It exists in a number of oxidation states, but only  $\text{Cr}^{3+}$  (non-toxic) and  $\text{Cr}^{6+}$  (toxic) are biologically and environmentally stable (Ducros, 1992). In solution state,  $\text{Cr}^{6+}$  may exist in three different ionic forms, such as hydro chromate ( $\text{HCrO}_4^-$ ), chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ). It may also exist as water-soluble complex anions and may persist in water, whereas in surface water rich in organic contents,  $\text{Cr}^{6+}$  exhibits a much shorter lifetime (Callahan, et al., 1979). The presence of each ionic form of chromium in solution is pH dependent (EPA, 1984). Chromium is present as insoluble  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (Fishbein, 1981) in soils and only a small part of it may be leached from soil.  $\text{Cr}^{6+}$  in soil tends to be reduced to  $\text{Cr}^{3+}$  by organic matter. It is mostly derived from human activities (mostly from chromate chemicals ATSDR (1993), in the environment.

$\text{Cr}^{6+}$  is much more toxic than  $\text{Cr}^{3+}$ , which is an essential nutrient required for normal energy metabolism and a dietary intake of 50-200  $\mu\text{g Cr}^{3+}/\text{day}$  is recommended. The estimated exposure dose of  $\text{Cr}^{6+}$  is limited to 0.57 mg/kg-day (Zhang and Li, 1987). Potassium dichromate has been reported as amplifier of some negative effects in organism (ATSDR, 1993, Susa, 1994). The bioavailability of chromium may be the single most important factor determining the toxicity of a specific chromium source (De Flora, 1987) and intracellular chromate reduction is required for chromium compounds to exert their genotoxic effects (ATSDR, 1993; O’Flaherty, 1996).

Due to the toxic behaviour of  $\text{Cr}^{6+}$ , potassium dichromate polluted site of Porto Romano, Albania, pointed as “Hot Spot Pollution” from UNEP/MAP (1992), was the object of our study. Aiming to get a simple method for  $\text{Cr}^{6+}$  speciation, spectrophotometric determination via 1.5–diphenylcarbazide, in aqueous, sediment and soil samples is validated whereas total Cr concentration was analyzed by AASF/and or AAS/ETA techniques.

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## Materials and Methods

### Instruments

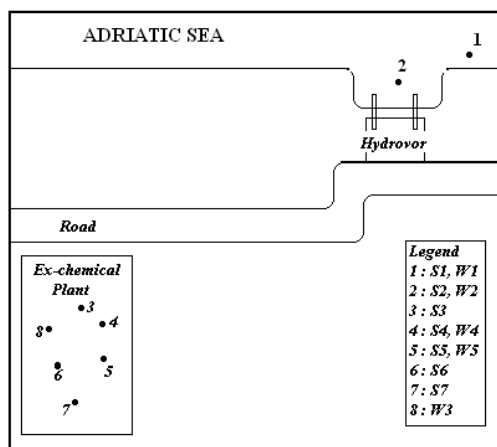
A spectrophotometer type Shimadzu UV2401 PC was used for spectrophotometric determination of  $\text{Cr}^{6+}$  in  $\lambda = 542 \text{ nm}$  using glass cells 1 cm and/or 2 cm. VARIAN 10+ atomic absorber is used for total Cr determination ( $\lambda = 357.9 \text{ nm}$ ,  $\Delta\lambda = 0.2 \text{ nm}$ , reducing  $\text{C}_2\text{H}_2/\text{Air}$  flame).

### Sampling area

Durres, the main harbour of Albania, is a coastal city with more than 150,000 inhabitants located in the central-western part of the country. About 6.5 km north of the city (in Porto Romano) a former chemical plant exists, extending on an overall surface of about 50 ha. It produced sodium dichromate, pesticides, such as Lindane (gamma-HCH), and other chemicals, until 1990. All production processes have been idle since the time and the plant's buildings have been totally destroyed. The area presents a "hot spot", comprising the remains of the Lindane and dichromate factory, a dumpsite nearby and a chemical waste storage site.

### Sampling sites

The sampling stations (five soil samples, S3 to S8, two seawater and sediment samples, S1, S2 and W1, W2, three surface water samples, W3 to W6) are shown in Figure 1.



**Figure 1.** Sampling stations

### Sampling Procedure

Sampling was implemented according to standard operation methods (APHA, 1998; ISO, 1999). Seawater/and or surface water samples were conserved on PET bottles and after filtration through OSMONIC INC, glass filter (1.0 micron) were acidified with 1ml/L  $\text{HNO}_3$  solution and stored at  $5^\circ\text{C}$ .

**Sediment samples:** The fractions smaller than 2 mm of the sediment samples were well homogenized by grinding in agate mortar until all material was going through a 200 mesh nylon sieve. The samples for chemical analyses were stored in airtight plastic vials until required for future use.

**Soil samples** were collected up to 15 cm deep from the surface, were air dried, sieved through a 2.0 mm screen, grounded and sieved through a 0.063 mm screen. The homogenized samples were stored in airtight pure plastic bags.

### Quality assurance of the data

A reference certified material (SDM/2-TM) was analyzed at the same time with sediment samples. Two inner standards ( $\text{Cr}^{6+}$  in seawater and soil samples) prepared in our laboratory, were analyzed at the same time with our samples of studied area. It could be noticed the data obtained were in good agreement with certified values.

**Methods of chemical analysis**

Total Cr concentration was analyzed by AAS technique. It is a routine analysis in our laboratory, so we are focused on the extraction of  $\text{Cr}^{6+}$  from soils and sediment samples, as well as in chemical method of its determination.

Aiming to get a simple method for  $\text{Cr}^{6+}$  speciation, spectrophotometric determination of  $\text{Cr}^{6+}$  via 1.5–diphenylcarbazide, in aqueous, sediment and soil samples is optimized.

**Spectrophotometric determination of  $\text{Cr}^{6+}$** 

The determination of metal species in soil solutions, methods are used which generally are based on a more profound analytical background (APHA, 1985). The purpose of this work was to standardize and optimize the procedure for quantification of  $\text{Cr}^{6+}$  content in water, sediment and soil samples based on conventional spectrophotometric methods of coloured  $\text{Cr}^{6+}$  - 1.5–diphenylcarbazide complex measured at 540 nm in acid solution (APHA, 1985). Optimization procedure was employed for determining the proper optimum operating conditions for both instrumental system and chemical variables. The proper operating conditions obtained were:

- 5 mg/l  $\text{Cr}^{6+}$ –1.5–diphenylcarbazide (2 ml 0.5%) solution measured in different concentration of acid solution caused constant adsorption for 0.1 to 0.5 M  $\text{H}_3\text{PO}_4$ /and or  $\text{H}_2\text{SO}_4$  medium ( $t=20$  min,  $\lambda=540$  nm).
- after the variation of quantity of diphenylcarbazide, the maximum adsorption was found for 0.5 to 4 ml 0.5% 1.5–diphenylcarbazide at  $\lambda=542$  nm (0.5 mg/l  $\text{Cr}^{6+}$  standard solution in 0.2 M  $\text{H}_3\text{PO}_4$  solution and measured after 20 min).
- The absorbance of standard solution via the time, using 1 ml 1.5–diphenylcarbazide 0.5, 0.1 M  $\text{H}_3\text{PO}_4$ /and or  $\text{H}_2\text{SO}_4$  was stable after 7 minutes
- Selectivity of the method was investigated through the interferences of  $\text{Fe}^{3+}$  ions (APHA, 1985, Llobat-Estellés, 2001).  $\text{Cr}^{6+}$  ions absorb on  $\lambda=373$  nm, whereas  $\text{Cr}^{6+}$  - 1.5–diphenylcarbazide complex have a strong absorption on  $\lambda=542$  nm, interfered from the presence of  $\text{Fe}^{3+}$  ions. For Fe/Cr ratio smaller than 500 in 0.2 M  $\text{H}_3\text{PO}_4$  and smaller than 10 in 0.2 M  $\text{H}_2\text{SO}_4$  medium, the interference of  $\text{Fe}^{3+}$  was negligible.
- The interference of  $\text{Fe}^{3+}$  was totally negligible by using 1.5 ml 5% NaF and 0.2 M  $\text{H}_3\text{PO}_4$  medium.

The optimal conditions of  $\text{Cr}^{6+}$  - 1.5–diphenylcarbazide measurements was:  $\text{H}_3\text{PO}_4$  0.2 M solution, adding 1.5 ml 5% NaF and 1 ml 0.5% 1.5–diphenylcarbazide, time of measurements after 7 minutes in  $\lambda=542$  nm. Avoiding the analyse interference blank solution was measured in the same time with samples.

Linearity of the response of the analyse was investigated through the linearity of calibration line, obtained from five standard solution, which showed a linear regression coefficients greater than 0.99 ( $y = 0.7991x + 0.0011$  with  $R^2 = 0.9995$ ). Beer's law is obeyed in the concentration range 0.05 - 5 mg/L of  $\text{Cr}^{6+}$  and the limit of detection was 4.7  $\mu\text{g/L}$  ( $l=1$  cm), which is low enough to allow determination of  $\text{Cr}^{6+}$  also in water samples.

**The extraction of  $\text{Cr}^{6+}$  from soil and sediment samples**

$\text{Cr}^{3+}$  is usually present in insoluble form  $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  in soils and only a small part of it may leached from soil, so we focused on the determination of  $\text{Cr}^{6+}$  (as most toxic form of Cr) in soil and sediment samples. Two different solutions, such as 0.5 M NaOH – 0.28 M  $\text{Na}_2\text{CO}_3$  (CEN/TR 14589: 2003) and  $\text{H}_3\text{PO}_4$  0.2 M (Dean, 2003) was used extracting Cr easy soluble from the contaminated soil, as well as from sediment samples.

To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied: (1) the extracting solution must solubilise all forms of Cr(VI), (2) the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III), and (3) the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI) (CEN/TR 14589: 2003). Under the alkaline conditions of the extraction, minimal reduction of Cr(VI) or oxidation of native Cr(III) occurs in the presence of carbonates. The presence of carbonates in the alkaline solution has been shown to precipitates Cr(III) to  $\text{Cr}(\text{OH})_3$  and Fe(III) to  $\text{Fe}(\text{OH})_3$ , suppressing the interferences to  $\text{Cr}^{6+}$ .

The quantification of Cr(VI) was performed colorimetrically with diphenylcarbazide by UV-VIS spectrophotometry and by AAS determination as an alternative method studying performance effectiveness of our determinations.

The sample is digested using 0.28 M Na CO<sub>3</sub> /0.5M NaOH solution without heating, via shaking in an electric shaker for 60 minutes to dissolve water soluble Cr(VI) and easy leached form of Cr(VI) and stabilize it against reduction to Cr(III).

For the characterization of each sample some additional analytical parameters, such as pH and Eh (mV) of the solution after the extraction was measured. The results are listed in table 1.

**Table 1.** Analytical parameters (pH and Eh (mV)) of the solution after alkaline extraction

Index	S1	S2	S3	S4	S5	S6	S7	S8
pH	13.17	13.17	13.22	13.17	13.2	11.68	11.75	11.75
Eh (mV)	-338	-348	-346	-350	-345	-264	-254	-265

Because final medium of Cr<sup>6+</sup> solution during calorimetrically determination with diphenylcarbazide by UV-VIS spectrophotometry is H<sub>3</sub>PO<sub>4</sub> (0.2 M), which is also recommended as a good leaching chemical (Dean J.R., 2003) of Cr<sup>6+</sup> from soil and sediment samples, we have tried it in our experiments. The results obtained via AAS analysis are given in table 2.

The examination of recovery of the extraction by addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> /and or PbCrO<sub>4</sub> to soil and sediment samples is used valuating the accuracy of the extraction procedure of both methods. The results are listed in table 3.

**Table 2.** Cr content in soil and sediment samples after extraction for 4 hours in an electric shaker

Sample	Easy extracted Cr (mg/kg, DW)	
	NaOH (0.5M)-Na <sub>2</sub> CO <sub>3</sub> (0.28M)	H <sub>3</sub> PO <sub>4</sub> (0.2 M)
S1*	6.05	4.23
S3**	1379.20	1316.40
S4**	378.54	349.80

\* sediment sample, \*\* soil sample

From the results given in table 2, we conclude 0.5 M NaOH–0.28 M Na<sub>2</sub>CO<sub>3</sub> solution results as the best extractor of Cr<sup>6+</sup> from soil and sediment samples. In both cases the results obtained from extraction with 0.2 M H<sub>3</sub>PO<sub>4</sub> are 30% to 4.6% lower than the results obtained with NaOH (0.5M)-Na<sub>2</sub>CO<sub>3</sub> (0.28M) extraction.

The same conclusion arrived from examination of recovery of Cr<sup>6+</sup> extraction from soil and sediment samples. The results obtained by using 0.2 M H<sub>3</sub>PO<sub>4</sub> extraction are 30% to about 17% lower than the results obtained by using NaOH (0.5M)-Na<sub>2</sub>CO<sub>3</sub> (0.28M) extraction for sediment samples. Better results achieved for soil samples contaminated with soluble form of Cr<sup>6+</sup>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, for both acid and alkaline extraction.

**Table 3.** The examination of recovery of the extraction

Index	Method	S2	+5 µg/l Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	+5 µg/l CrO <sub>4</sub> <sup>2-</sup>	+5 µg/l Cr <sup>3+</sup>	S4	+20 µg/l Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	+20 µg/l CrO <sub>4</sub> <sup>2-</sup>	+20 µg/l Cr <sup>3+</sup>	STDEV (Cr <sup>6+</sup> only)
Recovery (%)	Alkaline	100	104.7	99.8	0.60	100	105.3	101.04	1.10	2.13
	Acid	70	86	83	2.40	96.3	98.7	96.9	2.80	8.812

**Table 4.** Statistical treatment of the data

Index	Mean	F <sub>exp</sub>	F <sub>crit</sub>	t <sub>exp</sub>	t <sub>Crit</sub>
Recovery (%) (S2)	100.83	0.459	7.709	0.677	1.13
Recovery (%) (S4)	100.11				

The alkaline leaching method was found to be accurate as the recovery percent indicates a high precession with standard deviation less than 2.13 with the determination range of 0.02 to 0.5 mg  $\text{Cr}^{6+}$ /L in extracted solution. Applying F test to STDEV (see table 4) proofing the recovery results do not show significantly differences on STDEV to the estimated precision. The value obtained of  $t_{\text{exp}}=0.677 < t_{\text{crit}}=1.13$  (N=6, P=95%) proofed there is no systematic error exist at the given confidence level.

## Results and Discussion

### Hexavalent chromium content in water samples

The results of  $\text{Cr}^{6+}$  content in water samples obtained from spectrophotometric determination of  $\text{Cr}^{6+}$  after complex formation with 1.5–diphenylcarbazide are given in table 5.

**Table 5** Hexavalent chromium content in water samples (mg/l).

Index	W1*	W2*	W4**	W5**	W3***
$\text{Cr}^{6+}$	0.044	0.041	0.195	131.68	<LOD

\* Seawater sample, IN  $\mu\text{G/L}$  \*\* surface water sample, ground water sample, in mg/L.



**Figure 2.** View from W5 sampling site

$\text{Cr}^{+6}$  content in water samples differs significantly in three groups of samples:

1. It is not detected in groundwater sample (collected in a 5 m deep water shell inside territory of the plant,
2. It is in normal range in seawater samples, and
3. It is extremely high in surface water samples collected inside territory of the plant.

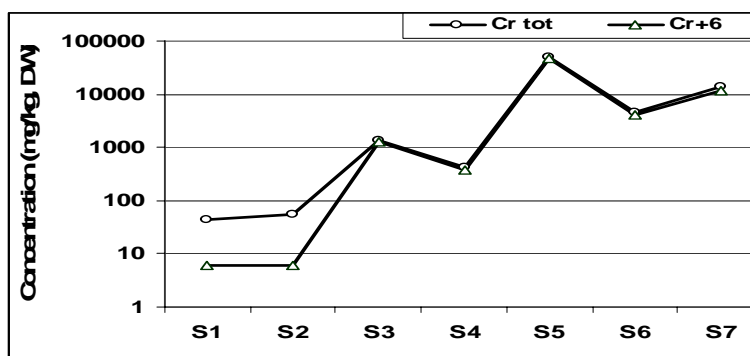
$\text{Cr}^{+6}$  content in water W5 sampling site is extremely high (131.68 mg/L). The origin of chromium there is from leaching (by raining) of the contaminated soils around W5 sampling site positioned in a small channel (see figure 1) inside the contaminated site. It is suggested gastrointestinal effects in humans may occur at an exposure level of 20mg/L  $\text{Cr}^{+6}$  (Zhang and Li, 987), but fortunately  $\text{Cr}^{+6}$  did not passed in drinking water (sample W3).  $\text{Cr}^{+6}$  content in seawater samples are very low and in the same level with the results obtained in our previous studies (Lazo *et al.*, 2003, Lazo *et al.*, 2000).

### Chromium content in soil and sediment samples

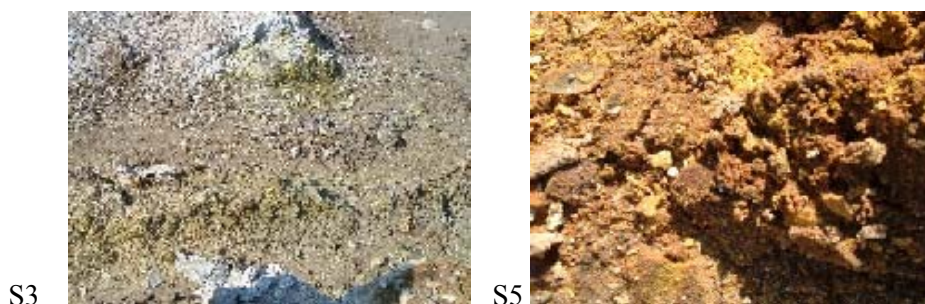
The results of total Cr, as well as  $\text{Cr}^{+6}$  content in soil and sediment samples are given in table 5.

**Table 5.** Cr content in soil and sediment samples (mg/kg, DW)

Index	S1	S2	S3	S4	S5	S6	S7
Cr tot	44.99	54.76	1380	420.25	48478.96	4485.28	13693.77
$\text{Cr}^{+6}$	6.06	6.05	1279.75	378.54	47682.6	4259.97	12986.83
Cr/ $\text{Cr}^{+6}$ (%)	13.47	11.04	92.74	90.08	98.4	94.97	94.84



**Figure 3.** Cr content in soil and sediment samples (mg/kg, DW).



**Figure 4.** Views from contaminated soils

As it is expected the content of total Cr in soil samples collected inside ex-chemical factory polluted from potassium dichromate was very high, otherwise in sediment samples it was very low, which indicate the chromium from the polluted area did not past in the sea. The most part of chromium in soil samples occurs in soluble form, whereas in sediment samples the most part of it is strongly bounded to the sediment, proofing again the conclusion.

### Conclusion

Satisfactory results obtained from alkaline (0.5 M NaOH – 0.28 M Na<sub>2</sub>CO<sub>3</sub>) leaching of Cr<sup>+6</sup> from soil and sediment samples, with a recovery up to 99.8%. Better results obtained for soil samples contaminated with soluble form of Cr<sup>6+</sup>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> than for sediment samples, for alkaline (0.5 M NaOH – 0.28 M Na<sub>2</sub>CO<sub>3</sub>) extraction (leaching recovery up to 98%).

The most part of chromium in soil samples occurs in soluble form (proofing the anthropogenic origin of it), whereas in sediment samples it is strongly bounded to the sediment, proofing the conclusion the chromium from the polluted area did not past in the sea.

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