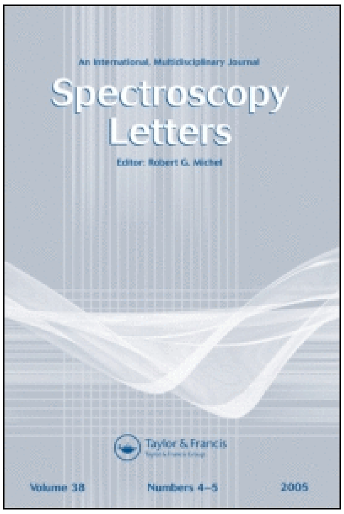

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ABSORPTION SPECTROSCOPY IN THE VISIBLE SPECTRAL RANGE OF TRIVALENT AND HEXAVALENT CHROMIUM IN DISTILLED WATER AND IN BUFFERS AT DIFFERENT pH VALUES

A. G. Mignani and A. Romolini*

IROE-CNR, Dept. of Optoelectronics and Photonics,
Via Panciatichi 64, 50127 Firenze, Italy

ABSTRACT

An exhaustive absorption spectroscopy study of both Hexavalent and Trivalent Chromium solutions in distilled water and in buffers in the acid range was carried out. Solutions in the wide 26 μg/L–520 mg/L concentration range were analysed in the visible spectral range by means of a conventional dual beam spectrophotometer equipped with 10 mm and 100 mm path length cuvettes in order to settle the minimum detectable concentration and the saturation limit.

Chromium detection at low concentration is of interest in environmental monitoring because of its carcinogenic risk, while high concentration monitoring is of interest in industrial process control, especially during sewage collection and recycling processes.

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*Corresponding author. E-mail: kajtr@tiscalinet.it

The presented absorption spectroscopy study was addressed to the implementation of an optical instrumentation for on-line Chromium detection making use of current optical fibre technology.

Key Words: Trivalent Chromium; Hexavalent Chromium; Absorption spectroscopy; Optical fibres

INTRODUCTION

Chromium is a naturally occurring element found in rocks, soils, plants, animals and in volcanic dust and gases. It has three main forms: Cr(0), Cr(III) and Cr(VI). Cr(III) compounds are stable and occur naturally in the environment, while Cr(0) does not occur naturally and Cr(VI) occurs only rarely. Environmental contamination due to Chromium has become a matter of serious concern because of its frequent use in industrial processes and other waste. Chromium is considered essential as well as toxic for human beings depending upon its speciation, in particular with respect to the oxidation state, and the doses and concentration levels involved.[1]

Trivalent and Hexavalent Chromium (Cr(III) and Cr(VI)) are the most common oxidation states of Chromium in the environment. Chromium is an important trace element in nutrition, but at the same time it is a toxic heavy metal, its toxicity depending on its valence state, Cr(VI) being significantly more toxic than Cr(III)[2] owing to its mobility in aqueous solutions. In fact, under usual environmental conditions, Cr(III) is poorly soluble whereas Cr(VI) is highly soluble. Cr(III) is relatively non-toxic at low concentrations (approximately one hundredth with respect to Cr(VI)), while, in trace concentrations, is an essential nutrient for human diet to maintain effective glucose, lipid and protein metabolism[3,4] and it is also useful for plants. In contrast, Cr(VI) is primarily produced by industrial processes and can diffuse through cell membranes and oxidise biological molecules with toxic results.[5] It has also been shown that Cr(VI) is a carcinogen even at trace concentration levels[6] and that skin contact with liquids or solids containing it may lead to skin ulcers. Cr(VI) has also been shown to be a human respiratory carcinogen in epidemiological studies[7,8,9] when humans are exposed to relatively high levels in the workplace. Therefore, speciative determination of Chromium is of particular interest and there has been considerable effort within industry and in the regulatory community to assess the potential cancer risk of workers exposed to relatively high levels of Cr(VI) in the workplace.[10,11,12]

Both Cr(VI) and Cr(III) are frequently used in industrial processes. Manufacturing of products or chemicals containing Chromium releases Chromium to the air, soil and water. Cr(III) and Cr(VI) enter the environment as a result of effluent discharge from a lot of industrial sources, including steel production, metal plating, leather tanning, spray painting operations and combustion sources, such as automobiles and incinerators. Most Chromium in water sticks to dirt particles that fall to the bottom; only a small amount dissolves. However, residual waste waters are rarely discharged directly into the sewers, because of the high pollution level. There are several companies that deal with sewage collection and on-line detection of Cr(III) and Cr(VI) performed during some stages of the recycling process. It is important to remark that Cr(VI) is easily reduced by dissolved sulfides and certain organic compounds with sulfydryl groups[13] that are sometimes present in the effluents of tanning industries. Cr(VI) in fresh water may also be reduced at considerable rate by organic matter such as tannic acid even in neutral pH regions.[14] On the other hand, Cr(III) is oxidised rapidly by a large excess of MnO_2 and slowly by dissolved oxygen at conditions approximating natural water.[14] As this interconvertion between Cr(III) and Cr(VI) may occur, the monitoring of Cr(III) in industrial effluent discharges becomes more important because it can reveal a higher emission of Cr(VI) with respect to those directly detected.

The aim of our work was to demonstrate the possibility of performing direct absorption spectroscopy of water samples by means of current optical fibre technology. Therefore, absorption measurements of Chromium solutions in distilled water and in buffers in the acid range were carried out. Solutions in the wide 26 μg/L–520 mg/L concentration range were analysed in the visible spectral range by means of a conventional dual beam spectrophotometer equipped with 10 mm and 100 mm path length cuvettes in order to settle the minimum detectable concentration and the saturation limit. Chromium detection at low concentration is of interest in environmental monitoring because of Cr(VI) carcinogenic risk even at trace concentrations, while high concentration monitoring is of interest in industrial process control, especially during sewage collection and recycling processes. A lot of Pollutants, interfering with Chromium, are usually present in industrial effluent discharges as well as other heavier residuals that may alter the pH state of the investigated pollutant even if it would be known. Consequently, we investigated the absorbance behaviour of Cr(III) and Cr(VI) at different pH values.

Sample Preparation and Measurement Acquisition and Processing

Cr(III) and Cr(VI) solutions in distilled water and in buffers at different pH values were prepared by using Chromium(III) Chloride

Hexahydrate ($CrCl_36H_2O$, molecular weight 266.45 g) and Potassium Dichromate ($K_2Cr_2O_7$, molecular weight 294.18 g) respectively, as a solute. The salts were chemical pure crystals provided by Merck (Darmstadt, Germany) and Riedel-De Haen AG Seelze (Hannover, Holland), respectively.

In the case of Cr(III) measurements, a highly-concentrated fundamental solution containing 520 mg/L was firstly prepared by weighing 1.3322 g of $CrCl_36H_2O$ and filling up the beker to half a litre. This fundamental solution was then sampled and diluted, in order to have six different concentrations of Cr(III): 520, 260, 52, 26, 5.2 and 2.6 mg/L. Solutions with Cr(III) concentration lower than 2.6 mg/L were not considered, because of their negligible absorption.

In order to obtain Cr(VI) solutions, a highly-concentrated fundamental solution containing 520 mg/L of Cr(VI) was firstly prepared by weighing 0.7355 g of $K_2Cr_2O_7$ and filling up the beker to half a litre. This fundamental solution was diluted, in order to have nine different concentrations of Cr(VI), which can be divided in two groups, relative to high and low concentrations, respectively: high concentrations: 260, 52, 26, 5.2 and 2.6 mg/L; low concentrations: 520, 260, 52 and 26 μg/L.

Absorption measurements were performed using a dual beam spectrophotometer Perkin Elmer, model Lambda 19, interfaced to a PC MS-DOS compatible, with the following settings: 250–850 nm spectral range, 240 nm/min scan speed, 2 nm spectrometer slit, quartz cuvettes with 100 and 10 mm path length. The spectra were processed by means of the Origin 5.0 software, which provides smoothing, peak searching, and fitting functions.

Cr(III) Absorption Measurements

Cr(III) solutions in water and in buffers were analysed by means of 100 mm path length cuvettes since absorption measurements performed with 10 mm path length cuvettes showed negligible absorbance levels. Figure 1 shows the measurement results. The spectra show two absorption peaks around 420 nm and 580 nm, respectively. Figure 2 shows the calibration curve at 420 and 580 nm, respectively, while Table 1 summarises the absorbance peak values. As expected, by diluting the fundamental solution by means of distilled water, the absorption peaks shift towards longer wavelengths.

Cr(III) buffered solutions with the same concentrations previously considered were prepared at constant values of pH. Buffers produced by Merck were used at the following pH values: 2, 3, 4 and 6. Figure 3 shows the measurement results at $pH = 2$: the spectra show two absorption peaks around 430 nm and 600 nm, respectively. Figure 4 shows the calibration

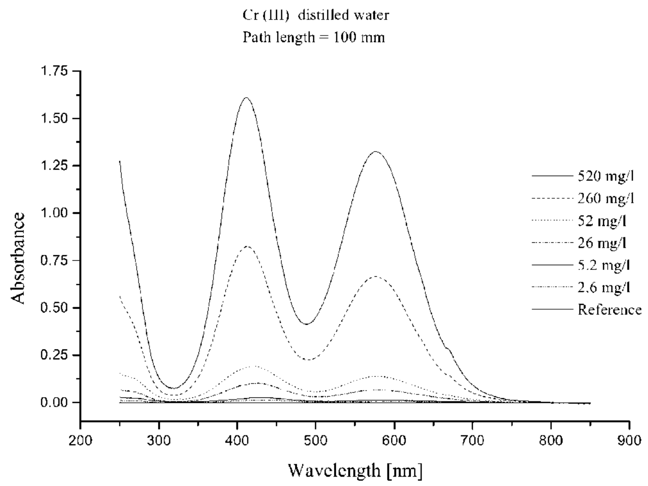

Figure 1. Absorption spectra of Cr(III) in distilled water.

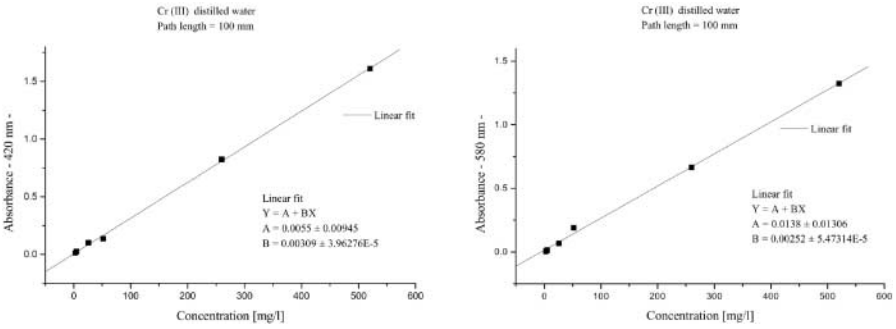

Figure 2. Calibration curve of Cr(III) in distilled water, at 420 nm (left) and 580 nm (right).

curves at 430 and 600 nm. Figure 5 shows the measurement results at pH = 3: the spectra show two absorption peaks around 415 nm and 580 nm, respectively. Figure 6 shows the calibration curves at 415 and 580 nm.

Figure 7 shows the measurement results at pH = 4: the spectra show two absorption peaks around 400 nm and 570 nm, respectively. Figure 8 shows the calibration curves at 400 and 570 nm. Figure 9 shows the measurement results at pH = 6: the spectra show two absorption peaks around 395 nm and 565 nm, respectively. Figure 10 shows the calibration curves at 395 and 565 nm.

Table 1. Cr(III) Peaks Wavelengths and Absorption Values vs. Concentration

Cr (III) Concentration (mg/l)	Distilled H_2O			
	1st Peak (nm)	Abs	2nd Peak (nm)	Abs
2.6	434	0.01325	597	0.00665
5.2	432	0.02697	583	0.01381
26	424	0.10155	579	0.0673
52	419	0.1368	578	0.19037
260	413	0.82386	575	0.66448
520	411	1.61011	576	1.32485

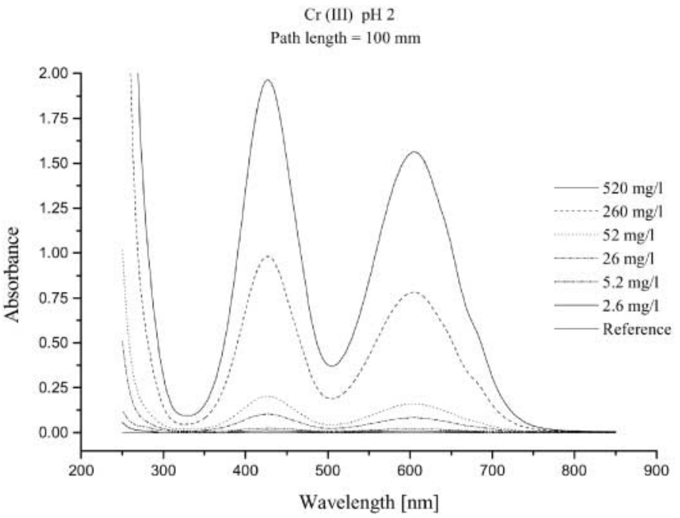

Figure 3. Absorption spectra of Cr(III) in buffered solution at pH = 2.

Cr(IV) Absorption Measurements

Measurements of high- and low-concentrated solutions in water and in buffers were performed with the long path quartz cuvette (100 mm). In addition, Cr(VI) highly-concentrated solutions with a shorter path length quartz cuvette (10 mm) were also analysed in order to avoid peak and plateau absorbance saturation at concentrations higher than 26 mg/L.

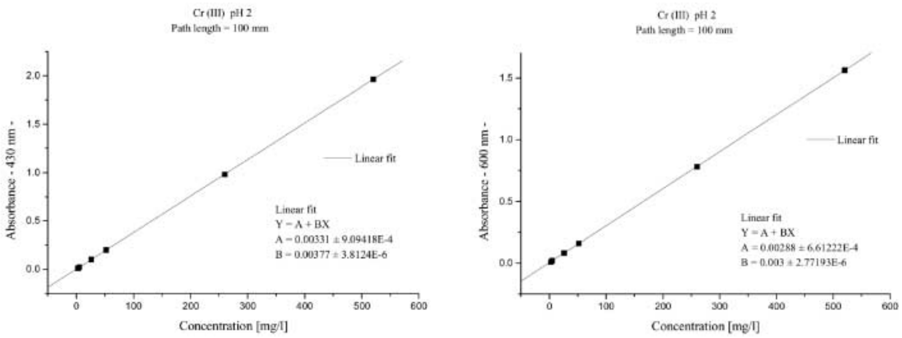

Figure 4. Calibration curves of Cr(III) in buffered solution at pH = 2, at 430 nm (left) and 600 nm (right).

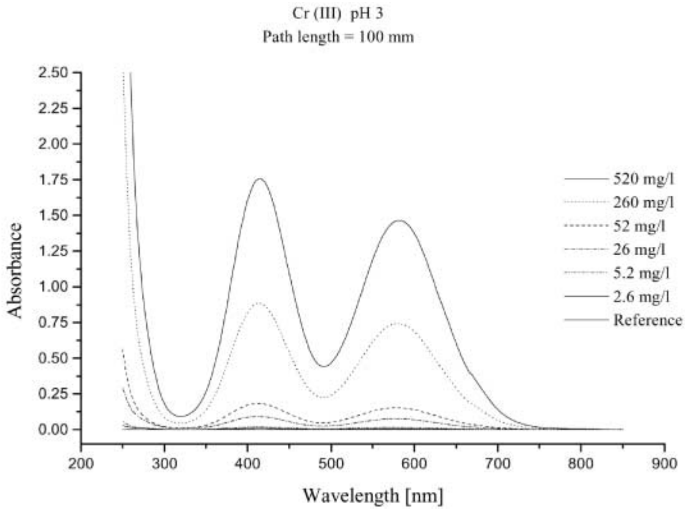

Figure 5. Absorption spectra of Cr(III) in buffered solution at pH = 3.

Absorption Measurements of Cr(VI) Solutions in Distilled Water and in Buffers: Long Path Measurements, High Concentration

The results of Cr(VI) measurements solutions in distilled water at high concentration performed with a quartz cuvette of 100 mm path length are shown in Fig. 11, while the same measurements performed in buffered solutions at pH 2 and 4 are shown in Figs. 12 and 13, respectively. An absorption peak at about 350 nm and an absorption plateau at about

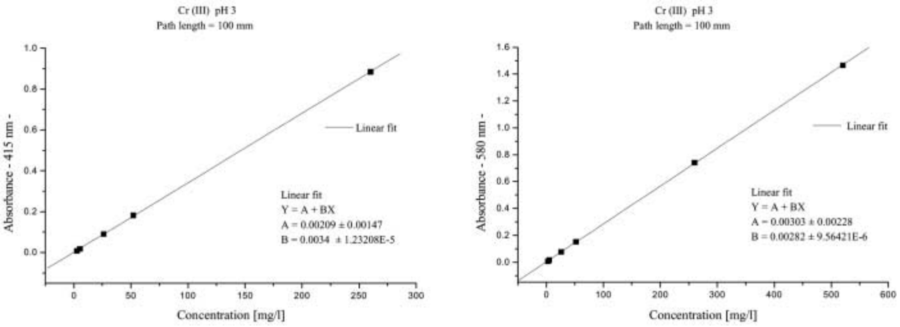

Figure 6. Calibration curves of Cr(III) in buffered solution at pH = 3, at 415 nm (left) and 580 nm (right).

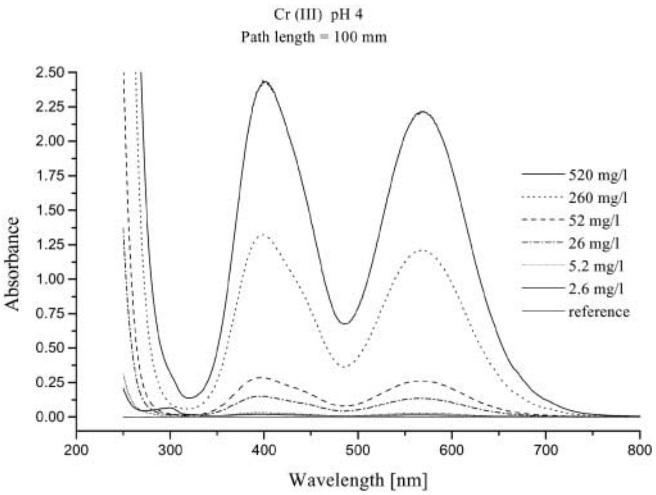

Figure 7. Absorption spectra of Cr(III) in buffered solution at pH = 4.

430 nm were detected, but the difference between water and buffered solutions was negligible, as well as the difference between spectra at different pH values. The only conclusion which can be drawn from these measurements is that for highly-concentrated solution (> 52 mg/L) a shorter path length must be used.

The results of Cr(VI) measurements in buffered solutions at pH = 6 are shown in Fig. 14. Higher values of peak wavelength (about 370 nm) and peak absorbance were detected with respect to the other tested pH values. Moreover, the absorption plateau at 430 nm was not present.

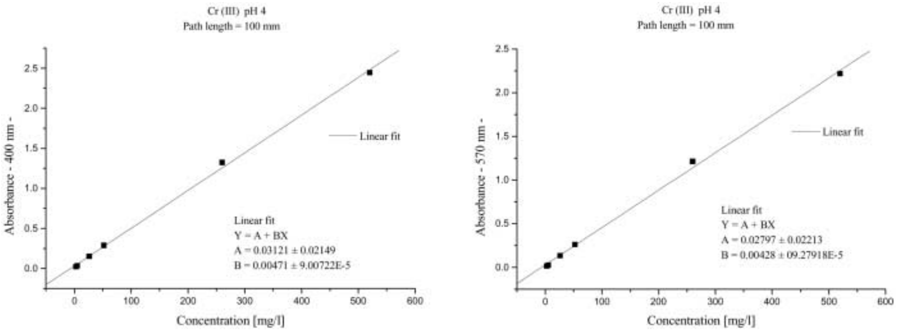

Figure 8. Calibration curves of Cr(III) in buffered solution at pH = 4, at 400 nm (left) and 570 nm (right).

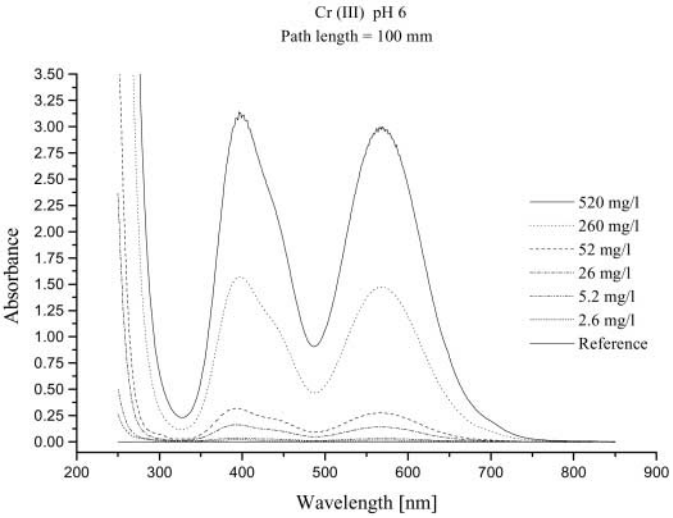

Figure 9. Absorption spectra of Cr(III) in buffered solution at pH = 6.

Absorption Measurements of Cr(VI) Solutions in Distilled Water and in Buffers: Short Path Measurements, High Concentration

In this subsection, Cr(VI) measurement results performed using a quartz cuvette of shorter path length (10 mm) are described. The other measurement parameters were the same of the previous subsection, i.e., high concentration solutions in distilled water and in buffers at pH 2, 4 and 6. As

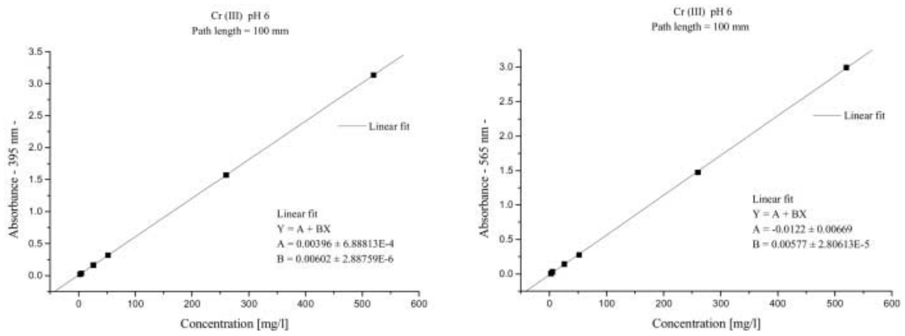

Figure 10. Calibration curves of Cr(III) in buffered solution at pH = 6, at 395 nm (left) and 565 nm (right).

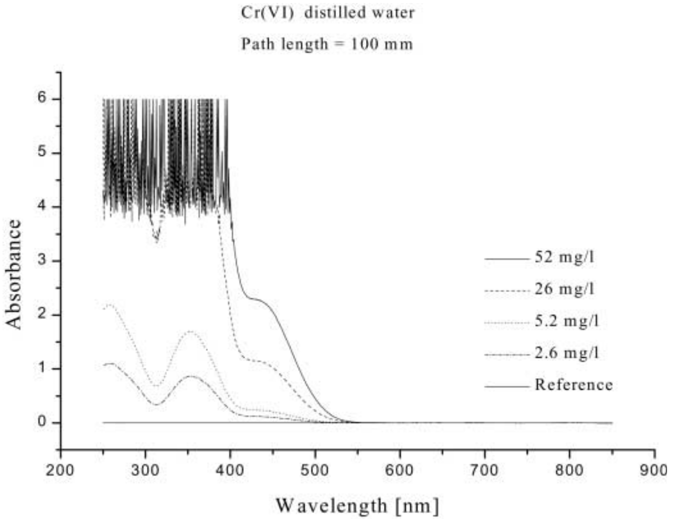

Figure 11. Absorption spectra of Cr(VI) in distilled water.

predicted by the Lambert-Beer law, absorption values decreased of a factor about 10 with respect to the same measurements performed with a path length ten times longer. Absorbance peak saturation at 26 and 52 mg/L and plateau saturation at 260 and 520 mg/L are avoided in these measurements.

The results of Cr(VI) measurements solutions in distilled water at high concentration performed with a quartz cuvette of 10 mm path length are shown in Fig. 15, while those of buffered solutions at pH 2, 4 and 6 are

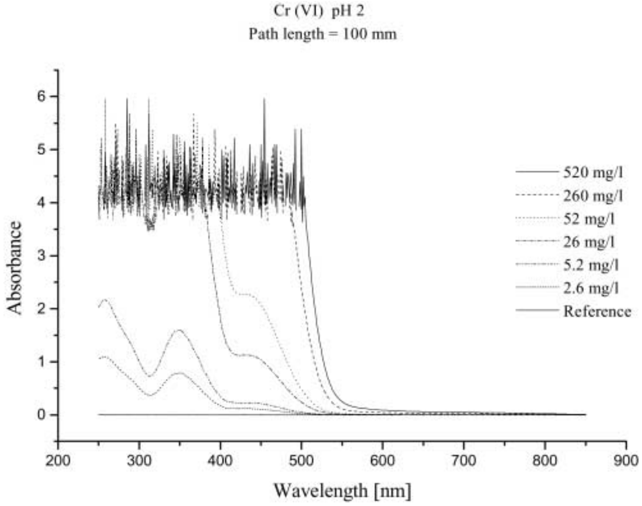

Figure 12. Absorption spectra of Cr(VI) in buffered solution at pH = 2.

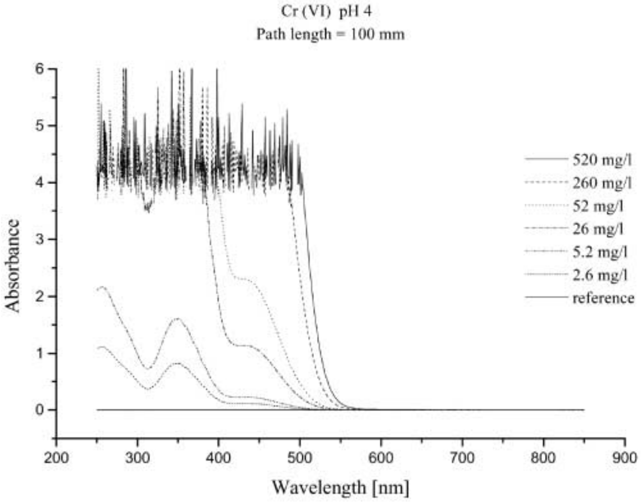

Figure 13. Absorption spectra of Cr(VI) in buffered solution at pH = 4.

shown in Figs. 16, 17 and 18, respectively. The spectral behaviour of solutions with respect to concentration and pH values is the same of the measurements shown in the previous subsection but with absorption values lower by a factor of about ten due to the use of the shorter path length.

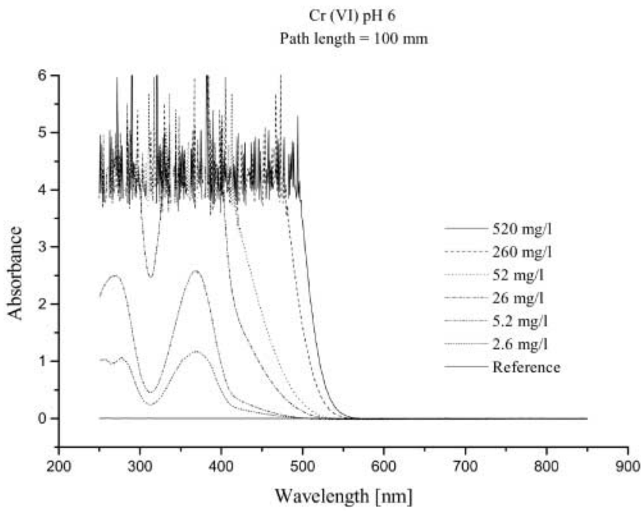

Figure 14. Absorption spectra of Cr(VI) in buffered solution at pH = 6.

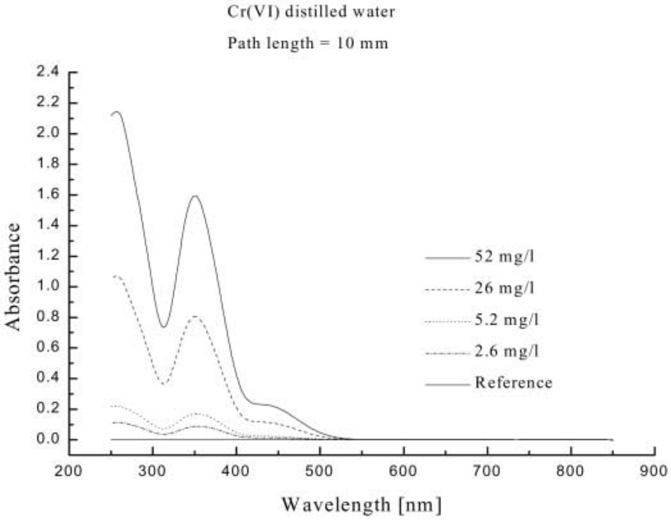

Figure 15. Absorption spectra of Cr(VI) in distilled water.

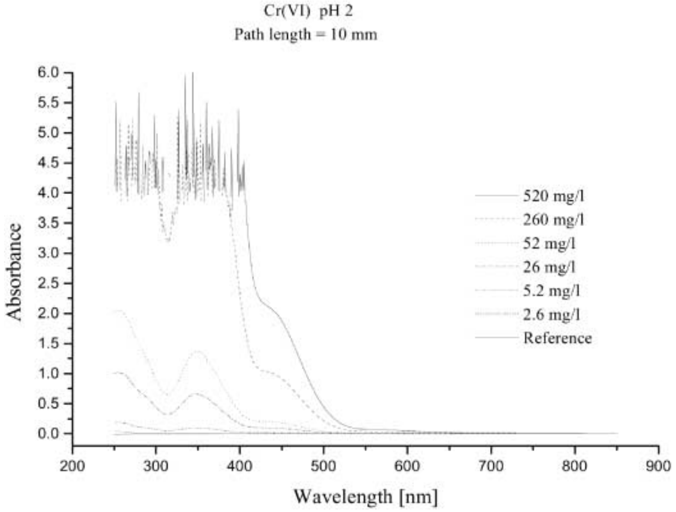

Figure 16. Absorption spectra of Cr(VI) in buffered solution at pH = 2.

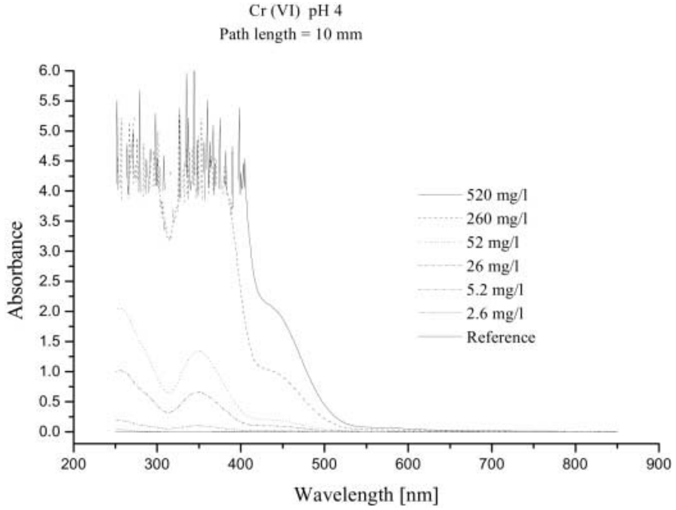

Figure 17. Absorption spectra of Cr(VI) in buffered solution at pH = 4.

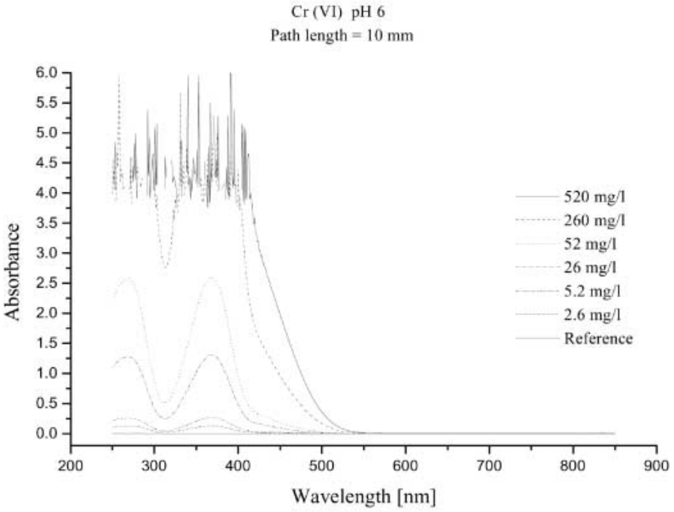

Figure 18. Absorption spectra of Cr(VI) in buffered solution at pH = 6.

Absorption Measurements of Cr(VI) Solutions in Distilled Water and in Buffers: Long Path Measurements, Low Concentration

The results of Cr(VI) measurements solutions in distilled water at low concentration (520, 260, 52 and 26 μg/L), performed with a quartz cuvette of 100 mm path length are shown in Fig. 19, while the same measurements performed in buffered solutions at pH 2, 4 and 6 are shown in Figs. 20, 21 and 22, respectively.

The absorption peak moved at the wavelength of about 360 nm for the solutions in distilled water and the buffered ones at pH values of 2 and 4, while the plateau absorbance level, at these low concentration values, was not clearly detectable. Lower peak absorbance levels, proportional to the lower concentration values of solutions, were measured, according to the Lambert-Beer law. Small differences in the absorbance levels between distilled water solutions and buffered solutions at pH 2 and 4 were detected, while the behaviour of buffered solutions at pH = 6 was the same of that detected at higher concentration values: higher values of peak wavelength (about 370 nm) and peak absorbance were detected with respect to the other tested pH values.

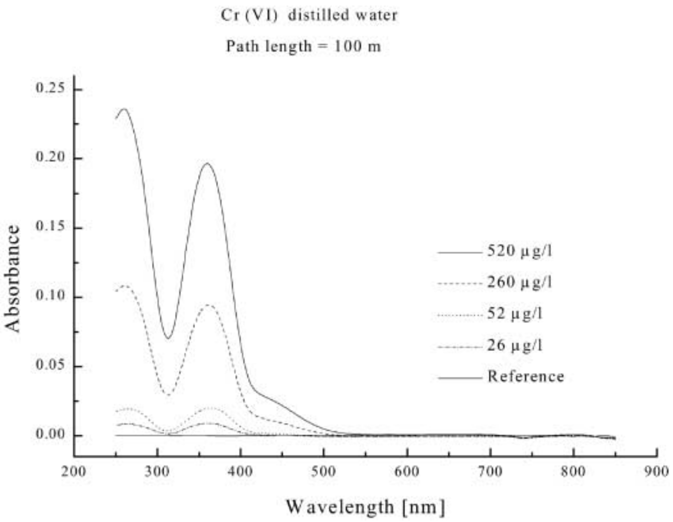

Figure 19. Absorption spectra of Cr(VI) in distilled water.

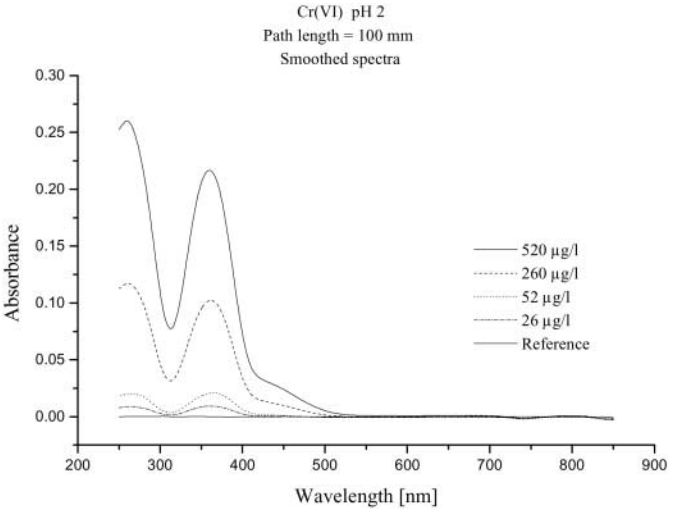

Figure 20. Absorption spectra of Cr(VI) in buffered solution at pH = 2.

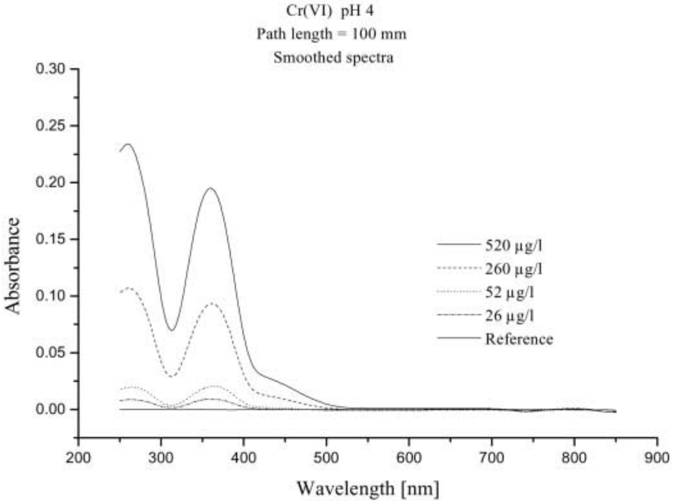

Figure 21. Absorption spectra of Cr(VI) in buffered solution at pH = 4.

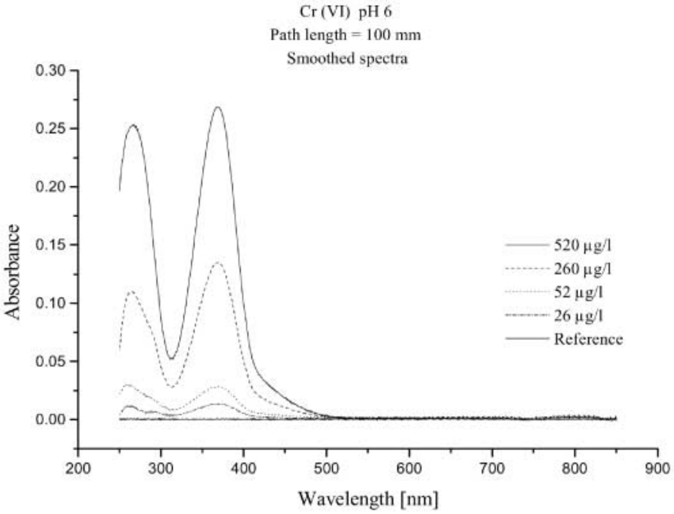

Figure 22. Absorption spectra of Cr(VI) in buffered solution at pH = 6.

DISCUSSION

Cr(III) measurements indicated that only concentrations higher than 26 mg/L can be clearly detected, and that the spectral position of the absorption peaks and the absorbance relative to each peak are different for solutions in distilled water or in buffers, and are pH-dependent. The behaviour of absorbance as a function of pH for all the concentrations considered was investigated for the two peaks.

Table 2A summarises the spectral position of absorption peaks and the relative absorbance at the various pH values. Table 2B, summarising the behaviour in water, is also given for comparison.

Figures 23, 24, 25 and 26 show the spectra at 26 mg/L, 52 mg/L, 260 mg/L and 520 mg/L, respectively, for the considered values of pH, compared to the spectrum in distilled water.

From the absorption measurements performed at the dual-beam spectrophotometer, some considerations can be drawn for the implementation of an instrumentation based on optical fiber technology:

- a basic instrumentation, able to detect Cr(VI) risk conditions can be implemented by exploiting the absorption plateau around 430 nm, together with the use of a long path length absorption probe (about 100 mm). In fact, a Cr(VI) solution with concentration of 260 μg/L gives a fairly measurable absorbance of 0.012. This basic instrumentation can make use of commercially available and cheap LED and PIN, as well as common optical fibres and connectors. The only optoelectronic component to be implemented is the long path length absorption probe, which is not available on the market.
- An advanced instrumentation able to give quantitative measurements of Cr(VI) in the 260 μg/L–52 mg/L concentration range can be implemented by exploiting the absorption peak around 360 nm, together with a short path length probe (about 10 mm). A long path length probe (about 100 mm) is not suitable for high concentration measurements, but it could be appropriate for measurements at very low concentrations, down to 26 μg/L. This advanced instrumentation can make use of source, microspectrometer and short path length probe which are commercially available. All-silica optics must be used. The same advanced instrumentation is also able to give quantitative measurements of Cr(III) in the 26 mg/L–520 mg/L concentration range by exploiting the absorption peak at 400 nm, together with a long path probe. In fact, a Cr(III) solution, in this concentration range

Table 2A. Cr(III) Peaks Absorption Behaviour as a Function of pH vs. Concentration

Cr (III) Conc. (mg/L)	pH 2				pH 3			
	1st Peak (nm)	Abs	2nd Peak (nm)	Abs	1st Peak (nm)	Abs	2nd Peak (nm)	Abs
2.6	430	0.01087	597	0.00891	412	0.00839	576	0.00649
5.2	426	0.0241	602	0.01954	414	0.01849	575	0.0152
26	427	0.10244	603	0.0819	412	0.09157	574	0.07678
52	428	0.20021	605	0.15915	411	0.18215	578	0.15289
260	427	0.9812	605	0.78176	414	0.88465	581	0.74221
520	427	1.96349	606	1.56314	415	1.75962	582	1.46601

Cr (III) Conc. (mg/L)	pH 4				pH 6			
	1st Peak (nm)	Abs	2nd Peak (nm)	Abs	1st Peak (nm)	Abs	2nd Peak (nm)	Abs
2.6	394	0.02145	558	0.01685	392	0.01753	564	0.0159
5.2	394	0.03386	569	0.0292	396	0.03578	567	0.03088
26	394	0.15156	567	0.13639	392	0.16154	566	0.1416
52	398	0.28732	569	0.26194	393	0.31688	567	0.27418
260	399	1.32361	567	1.21126	396	1.56981	569	1.47205
520	399	2.44332	570	2.2186	396	3.133	569	2.99521

Table 2B. Summary of the Spectral Position of Absorption Peaks and the Relative Absorbance in Distilled Water

Cr (III) Concentration (mg/L)	Distilled H_2O			
	1st Peak (nm)	*Abs*	2nd Peak (nm)	*Abs*
2.6	434	0.01325	597	0.00665
5.2	432	0.02697	583	0.01381
26	424	0.10155	579	0.0673
52	419	0.1368	578	0.19037
260	413	0.82386	575	0.66448
520	411	1.61011	576	1.32485

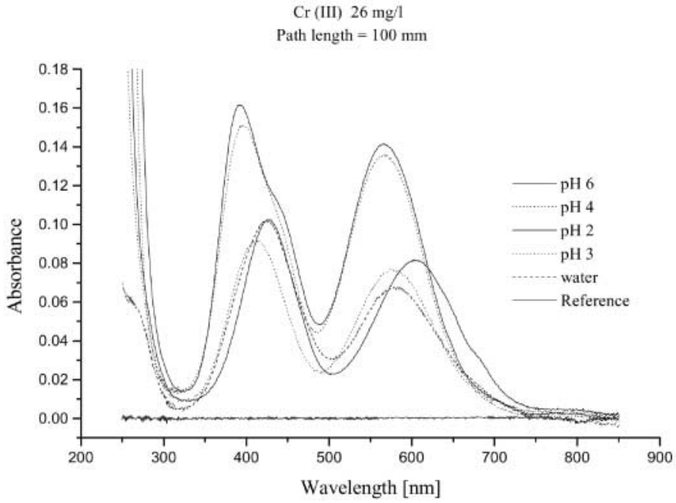

Figure 23. Spectra at the fixed concentration of 26 mg/L, for all the considered values of pH, compared to the spectrum in distilled water.

and for acid pH values, gives a measurable absorbance between 0.01 and 3.13.

CONCLUSIONS

A spectrophotometric absorption study of Cr(VI) and Cr(III) solutions in the 26 μg/L—520 mg/L concentration range in distilled water and in

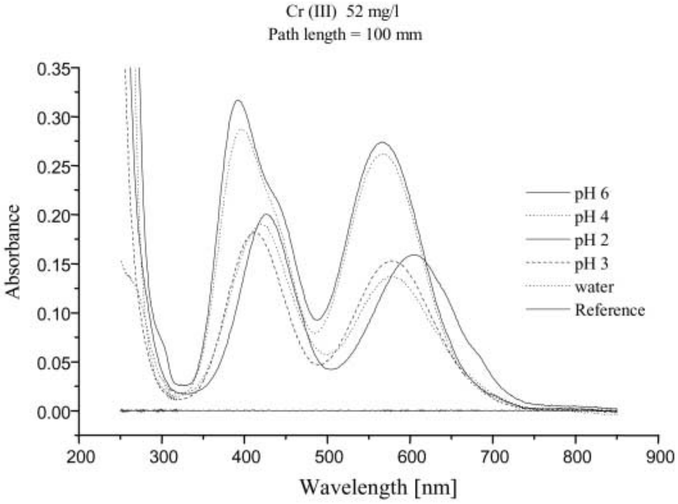

Figure 24. Spectra at the fixed concentration of 52 mg/L, for all the considered values of pH, compared to the spectrum in distilled water.

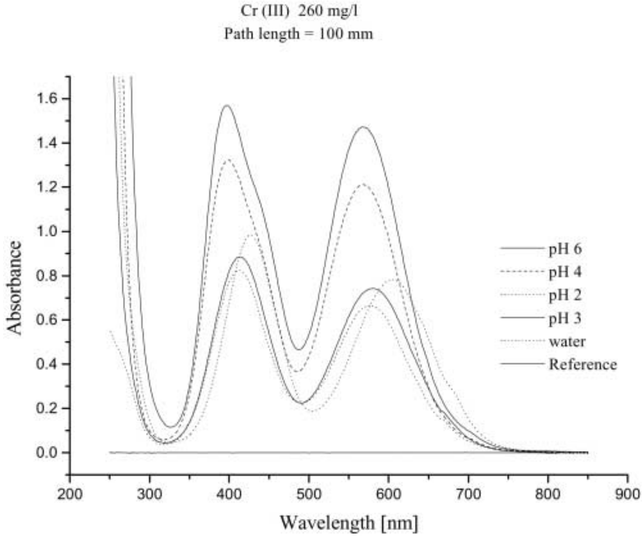

Figure 25. Spectra at the fixed concentration of 260 mg/L, for all the considered values of pH, compared to the spectrum in distilled water.

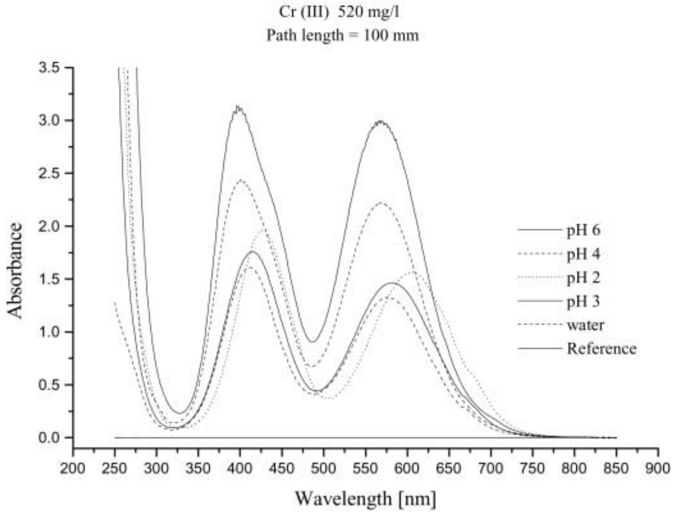

Figure 26. Spectra at the fixed concentration of 520 mg/L, for all the considered values of pH, compared to the spectrum in distilled water.

buffers at different values in the acid range, was performed. Measurements were carried out with different absorption path lengths by using 100 mm and 10 mm quartz cuvettes in order to cover the wide range of concentrations investigated. The lower and upper concentration limits were chosen as the minimum detectable and the saturation limit respectively, according with the used experimental set-up. All the measurements were in agreement with the Lambert-Beer law. Different spectral behaviour was detected at different pH values for Cr(III) measurements, while no significance difference was shown for Cr(VI).

All the measurements carried out demonstrated the possibility of performing direct absorption spectroscopy of water samples using current optical fibre technology. Other measurements are in progress for the analysis of mixtures, containing not only Chromium, but also other pollutants having interfering absorption spectra with Chromium, such as Sulphide and Manganese Sulphate or Chloride. The spectra of Chromium, Sulphide, Manganese Sulphate, Manganese Chloride and of their mixtures in known proportions will be processed by means of an artificial neural network software for individual compound detection. After the instruction, the neural network will be able to distinguish the contribution of single pollutants, whose spectra may also totally overlap, from the complex spectra of waste waters taken during some stages of the industrial recycling process.

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REFERENCES

1. Nirago, J.O.; Niebor, E. In *Chromium in Natural and Human Environment*; Wiley: New York, 1988.
2. Moore, J.W.; Ramamoorthy, S. In *Heavy metals in Natural Waters*; Springer: New York, 1984.
3. Kortenkamp, A.; Casadevall, M.; Faux, S.P.; Jenner, A.; Shayer, R.O.J.; Woodbridge, N.; O'Brien, P. Arch Biochem. Biophysi. **1996**, *329* (2), 199.
4. Brauer, S.L.; Wetterhahn, K.E. J. Am. Chem. Soc. **1991**, *113*, 3001.
5. Kortenkamp, A.; Ozolins, Z.; Beyersmann, D.; O'Brien, P. Mutat. Res. **1989**, *216*, 19.
6. Langard, S.; Norseth, T. Br. J. Ind. Med. **1975**, *32*, 72.
7. Sheehan, P.; Ricks, R.; Ripple, S.; Paustenbach, D. Am. Ind. Hyg. Assoc. J. **1992**, *53*, 57.
8. Hayes, R.B. In *Biological and Environmental Aspects of Chromium*; Elsevier: Amsterdam, 1982.
9. Dillon, C.T.; Lay, P.A.; Bonin, A.M.; Dixon, N.E.; Collins, T.J.; Kostka, K. Carcinogenesis. **1993**, *14* (9), 1875.
10. Wang, J.; Marshall, W.D. Analyst. **1996**, *121*, 817.
11. Katz, S.A.; Salem, H. In *The Biological and Environmental Chemistry of Chromium*; VCH: New York, 1994.
12. De Andrade, J.C.; Roca, J.C.; Baccan, N. Analyst. **1985**, *110*, 197.
13. Moorey, J.W.; Ramamoorthy, S. In *Heavy metals in natural waters*; Springer: New York, 1983.
14. Osaki, S.; Osaki, T.; Nishino, K.; Takashima, Y. Nippon Kagaku Kaishi. **1980**, *11*, 1802.

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