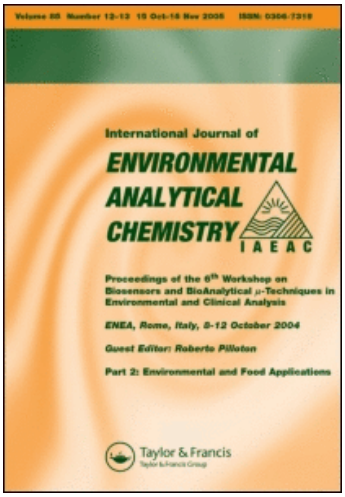

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Speciation of Chromium in Waters by Coprecipitation-AAS*

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An analytical scheme for chromium speciation by coprecipitation with lead salts-AAS is described. It allows the partitioning of the total concentration of the metal into four fractions: Cr(VI), free Cr(III), complexed Cr(III), and particulate metal. First, the sample is filtered through 0.45 μ; filters are treated with diluted nitric acid to dissolve and determine the particulate chromium. The filtrate was used for three determinations: one of them on the acidified sample, without any treatment; another one after a coprecipitation with lead phosphate at pH 6–7 (both valency states are scavenged); and finally, the other one after a coprecipitation with lead sulphate at pH 3 (only Cr(VI) is collected).

GFAAS has been used in all measurements using standards of $K_2Cr_2O_7$ in 0.1 N HNO_3. It is confirmed that the responses of both valency states do not show significative statistical differences, using coated as well as ordinary tubes.

In our opinion, this scheme shows some important advantages: the concentration of Cr(VI), the species whose determination has more interest, is calculated directly, not by difference; in both coprecipitations the carriers do not interfere in the later measurement by GFAAS; the same standard solutions are used in the four necessary determinations for each sample, and it is not necessary to apply the standard additions method because the cation has been already scavenged from the original matrix; finally, the analytical procedure is relatively simple in comparison with the usual tedious laboratory work that is required by this kind of study.

The scheme described above has been successfully applied to 33 samples from the Sau reservoir.

KEY WORDS: Chromium speciation, coprecipitation lead salts, atomic absorption spectrometry.

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INTRODUCTION

The impact of chromium on the environment and on biological systems has been the object of many studies since it seems that it presents carcinogenic effects through mechanisms in which Cr(III) intervenes. On the other hand, the (VI) valence of the element, being more soluble and consequently more readily available and more easily conveyed into cells, is the valence presenting a high degree of danger. The change in the valence of chromium in nature, be it by oxidation to Cr(VI) or by reduction to Cr(III), may occur through chemical or biochemical mechanisms. Therefore, many speciation studies of this metal in the environment have been carried out.

The subject of the speciation of chromium in water has been treated by several authors experimentally as well as from thermodynamical considerations, indicating that largely, in oxygenated waters hexavalent chromium prevails over the trivalent one, while in anoxic zones and in the presence of organic matter in a degradation process, the presence of Cr(III) is favoured. All the same, the results obtained in diverse studies are, in many cases, not very concordant and even contradictory. This is mainly attributed to the utilization of techniques of the species considered which are not sufficiently selective, and to the evolution of the samples between sampling and the chemical analysis, as well as, to the fact that the presence of organic compounds of chromium may not have always been taken into account.

The methods of analysis of Cr(III) and Cr(VI) published in the bibliography usually develop into two steps: separation of one or both the considered species from the original matrix, and then the step of determination of each one of them. A great variety of techniques of separation have been utilized; among them there may be pointed out the use of chelating and ion-exchange resins, the chelation-extraction with organic solvents, and the techniques of coprecipitation. As to the measurement techniques, AAS— although it does not permit the differentiation of valence states, yet is applicable whenever a step of separation precedes— competes advantageously with the classical method of colorimetry with diphenylcarbazide. Neutron activation, γ-spectrometry and, lately, ICP are also utilized.

In the present work, a speciation scheme for Cr(III)–Cr(VI) in waters is described, based on the selective coprecipitation as separative step, technique which permits the speciation process without excessive sample manipulation, and the Graphite Furnace Atomic Absorption Spectrometry (GFAAS) as measurement technique, as consequence of its known applicability due to its high sensitivity and the experience we have acquired in its use.

As regards the coprecipitation step, the utilization of diverse coprecipitation reagents for the preconcentration and/or speciation of chromium has been described in the bibliography, such as the hydroxides of Fe(III)[1,2] and Al(III)[3] for the collection of Cr(III); the sulphates of lead[4,5] and barium[6] for Cr(VI); and the hydroxides of Fe(II)[2] and Bi(III),[1] and lead phosphate[5] for both oxidation states. Iron hydroxides have been most used: the use of $Fe(OH)_3$ was already proposed in 1967 by Chuecas and Riley[7] for the preconcentration of Cr(III) in sea water. However, both of these compounds present the draw-back that, if the determination is carried out either by colorimetry with diphenylcarbazide or by AAS, a serious problem of interference is encountered. This is due to the presence of large amounts of iron, which require the elimination of the interference by alkaline fusion, ion-exchange, or chelation-extraction, thereby notably complicating the analytical process and increasing the contamination risk. In addition, the coprecipitation of Cr(III) with $Fe(OH)_3$ presents the draw-back that Cr(VI) may be partially absorbed by the precipitate. All of this, together with the fact that iron salts are usually impurified with high contents of chromium and that its purification to the level required in these studies is frankly difficult, made us decide for the utilization of lead salts, concretely lead sulphate for Cr(VI) and lead phosphate for both valence states.

As to the determination of chromium by GFAAS, the mechanisms proposed in the bibliography[8] coincide in suggesting that Cr(III) and Cr(VI) produce identical signals, since both oxidation states lead to the formation of Cr_2O_3 in the ashing step of the heating program. On the other hand, Martin and Riley[4] point out having observed a different behaviour for the two species, although they do not furnish any information to the point. Therefore, an experimental study will have to be made on the signals for both valence states at the measurement conditions to be adopted.

EXPERIMENTAL

Reagents and instrumental

Cr(VI) standards were prepared from a solution of 1000 ppm in 0.1 N HNO_3, and those of Cr(III) from the latter by reduction with hydrogen peroxide. All the reagents used have been of analytical grade except HNO_3, which was Merck Suprapur.

The determinations have been carried out in a Perkin Elmer model 4000 atomic absorption spectrophotometer, with graphite furnace HGA-400, and autosampler AS-40. The heating programme used was: drying at 100°C, ashing at 1000°C, and atomization at 2700°C for ordinary tube and at 2500°C for coated tube. A background corrector with deuterium lamp, and nitrogen as inert gas, were used; its flux was interrupted 5 seconds before the beginning of the atomization step. The experience was done at constant injection volume of 20 μl, and the signal is registered in peak height.

Speciation scheme

In Figure 1, the proposed speciation scheme is shown, which permits the partitioning of the total metal concentration into four fractions: Cr(VI), free Cr(III), complexed Cr(III), and particulate Cr.

To start with, the sample is vacuum filtered through a precleaned 0.45 μ Millipore filter. The speciation scheme is based on four independent processes, three of them (A, B and C) on the filtrate, and one (D) on the particulate matter retained on the filter. Both coprecipitations described here are carried out on the filtrate, and a third measurement is done on the acidified sample (0.5 ml conc. HNO_3/50 ml sample) without any manipulation; the particulate metal is determined after the treatment of each one of the filters with 20 ml of 1:10 HNO_3 at 55–60°C during ninety minutes and filling up to the desired volume.

Coprecipitation with sulphate: 50 ml of sample are placed in a stoppered centrifuge tube and the pH is adjusted to 3 by means of a pH meter with diluted HNO_3. 0.5 ml of 0.2 M lead nitrate and 0.5 ml of 0.2 ammonium sulphate are added. The whole is maintained under mechanical agitation during twenty minutes, then centrifuged under increasing speed up to 2000 rpm during ten minutes, and then

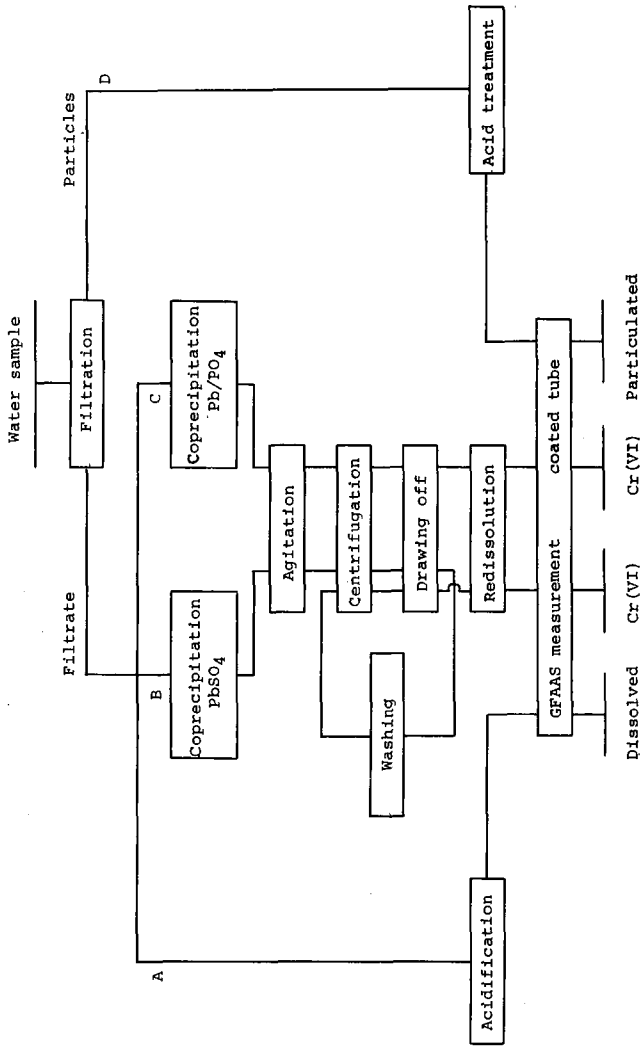


Figure 1 Speciation scheme.

decanted. Ten millilitre of washing water, to which a few drops of solution of lead nitrate have been added, are introduced, and then the whole is again centrifuged in the same way as before, and decanted anew. Then, the precipitate is dissolved with 1 ml of conc. HNO_3 and made up to 10 ml with water.

Coprecipitation with phosphate: 50 ml of sample are placed in a stoppered centrifuge tube and 0.1 ml of 1:1 HNO_3 is added, as well as 0.2 ml of 0.2 M lead nitrate, and 0.3 ml of 0.04 ammonium phosphate. Then 3–4 drops of 0.1% methyl red are added, and the whole is manually agitated and 2 N NH_3 added till a change in the indicator is observed. It is kept under mechanical agitation during 20 minutes, centrifuged under increasing speed up to 2000 rpm during ten minutes, and decanted. Then the precipitate is dissolved and the volume is made up to 10 ml with 0.1 N HNO_3.

In both coprecipitations, when the samples present, *a priori*, high concentrations of the species to be determined, an adequately smaller volume of them may be taken in each case, and made up to 50 ml with distilled water.

All the determinations, four for each sample, are carried out through GFAAS measurement, and the concentrations of the diverse species are calculated from those determinations, taking into account the concentration or dilution factors of each sample and process.

RESULTS AND DISCUSSION

From the study about the signals of Cr(VI) and Cr(III) by GFAAS it can be inferred that the absorbance signal is practically the same for the two species, whether in an uncoated tube or in a coated one. We have also verified that the coated tubes provide a sensitivity of the order of five times higher (Figure 2), and do not present memory effects. On that account, all the analytical determinations are carried out utilizing Cr(VI) standards in a coated tube. It is important to point out that since both Cr(VI) and Cr(III) standards have been prepared from the same stock $K_2Cr_2O_7$ solution, and that the excess of reducing agent utilized for the preparation of the trivalent chromium standards is easily eliminated by boiling, the possible causes of variability, alien to the valence state of the metal, are eliminated.

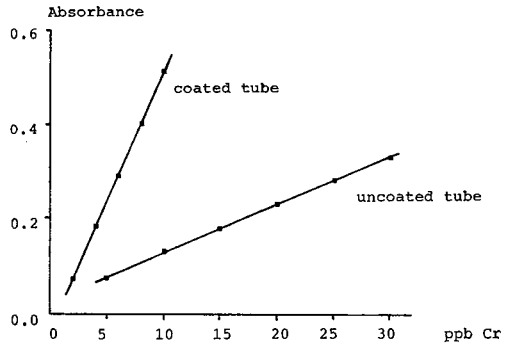


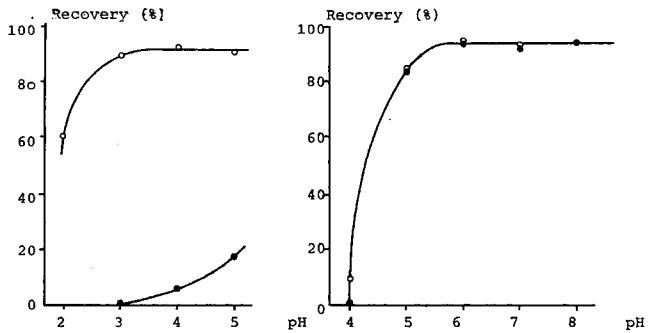
Figure 2 GFAAS signal of Cr (injection volume 20 μl).

After a previous study of the optimal conditions, especially with reference to the pH (Figures 3 and 4), the following recovery percentages for 0.1 and 0.5 μg of chromium have been obtained:

a) Coprecipitation of Cr(VI) as $PbCrO_4$ with $PbSO_4$ (30 mg) at pH 3: 89%.

b) Coprecipitation of Cr(III) as $CrPO_4$ and of Cr(VI) as $PbCrO_4$ with Pb/PO_4 (5 mg) at pH 6: 95% for both species.

The recoveries obtained are similar to those shown in the work of Han-Fei Zhang and coworkers[5] from whom the coprecipitation conditions have been taken, although the procedure we have utilized



Figures 3 and 4 Recoveries of coprecipitation of Cr(III) (●) and Cr(VI) (○) with $PbSO_4$ (Figure 3) and Pb/PO_4 (Figure 4).

is carried out with smaller sample (50 ml) and carrier amounts, in the order of a few mg. This permits utilizing centrifuging for separation of the precipitate from the original matrix and so avoid cumbersome filtration. On the other hand, the analytical determinations are carried out by GFAAS with a previous acid redissolution of both precipitates, and not by direct γ-spectrometry.

In our opinion, the scheme proposed presents some advantages. To begin with, the concentration of Cr(VI), the most interesting species, is calculated directly, not by difference as it is done in some schemes where the concentration of these species is calculated from the difference between the signal corresponding to both valence states taken together and that produced by trivalent chromium. This latter calculation may lead to inexact results in samples in which Cr(VI) may exist in a minor proportion. It is also noted that in both coprecipitations, concentration factors are obtained of up to 5, and that the carriers do not interfere in the determination by GFAAS. On the other hand, in the four measurements per sample, the same standards are used, and it is not necessary to apply the standard additions method since the cation has been previously scavenged from the original matrix. Finally, the analytical procedure is comparatively simple with the usual laboratory work required by this type of studies. To this simplicity contribute in a special manner the two coprecipitation processes, which are wholly developed within 50 ml centrifuge tubes containing a few mg of precipitate, and requiring a minimal sample manipulation.

The proposed speciation scheme has been applied to 33 samples from the Sau reservoir and corresponding to three samplings. This reservoir is a part, together with those of Susqueda and El Pasteral, of the hydrographic system of the Ter river providing Barcelona city with drinking water supply, and presents good possibilities for a study of speciation of chromium since it gathers the waters of Gurri river in which the tanneries situated in the town of Vic discharge their wastewaters. Nevertheless, we would like to point out the fact that it is not our intention to reach conclusions upon the behaviour of the metal in this system—for which purpose a much larger number of samplings would be required—but just to verify the applicability of the method of speciation proposed in this paper.

Five sampling sites have been selected (Figure 5): Gurri river between Vic and Roda de Ter; river near Manlleu; Roda, a few

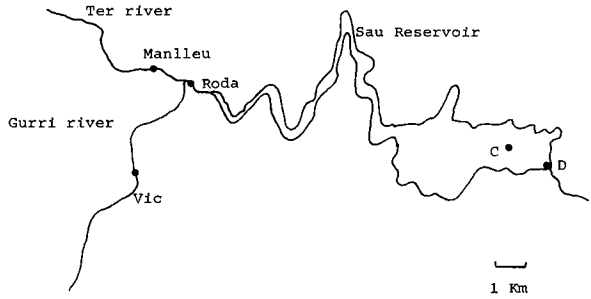


Figure 5 Location of the sampling points.

meters downstream from the merging of the Gurri and Ter rivers; center or zone of maximal depth of the reservoir (C), where a depth profile is carried out; and lastly, beside the dam (D), at the depth of the habitual outlet.

In Table I, the results obtained in the sampling of June 1985 are shown for illustration. Altogether, the three samplings confirm the

Table I Results of analyses for chromium speciation (μg/l)

Sample	Dissolved Cr				Total Dissolv. Cr	Total Partic. Cr	Total Cr
	Cr(VI)	Cr(III)					
		Free	Complex.	Total			
C-0	0.4	0.5	0.7	1.2	1.6	0.7	2.3
C-2	0.4	0.6	0.6	1.2	1.6	0.7	2.3
C-5	0.5	0.3	0.8	1.1	1.6	0.7	2.3
C-10	0.4	0.3	1.0	1.3	1.7	0.8	2.5
C-20	0.4	0.6	0.7	1.3	1.7	1.0	2.7
C-30	0.5	0.9	0.5	1.4	1.9	1.7	3.6
C-40	0.4	0.7	0.2	0.9	1.3	2.0	3.3
C-52	1.3	4.2	2.8	7.0	8.3	40.0	48.3
D-36	0.4	1.2	1.1	2.3	2.7	1.7	4.4
Roda	2.8	3.2	2.5	5.7	8.5	82.0	90.5
Manlleu	0.1	0.2	0.2	0.4	0.5	1.4	1.9
Vic	7.6	57.4	4.0	61.4	69	4585	4654

fact that Vic is a very notable contamination source. Comparing the values obtained in Roda with those from near Manlleu, upstream from the Gurri-Ter confluence, there may be inferred that a higher percentage than the 95% of the chromium reaching the reservoir comes from Vic. In the Gurri river the metal is largely from the reservoir, while they permit the evaluation of the habitual concentration levels of the diverse species, they do not permit to reach conclusions as to the distribution of the metal in it.

In Table II the precision and detection limits obtained are shown for the four procedures in the scheme proposed. The precision is expressed in terms of variation coefficient, and the detection limit as the concentration corresponding to twice the standard deviation of the blank. In both cases six repetitions have been carried out. For the particulate metal, a volume of 250 ml of filtered sample is assumed.

Table II Precision and detection limit

Process	Detection limit μg/l	Precision %
A	0.04	1.9
B	0.03	6.2
C	0.09	4.3
D	0.15	9.3

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References

1. E. Nakayama *et al.*, *Anal. Chim. Acta* **131,** 247 (1981).
2. R. E. Cranston and J. W. Murray, *Anal. Chim. Acta* **99,** 275 (1978).
3. M. Hiraide *et al.*, *Anal. Chim. Acta* **81,** 185 (1976).

4. T. D. Martin and J. K. Riley, *Atom. Spect.* **3,** 174 (1982).
5. H. F. Zhang *et al.*, *Anal. Chim. Acta* **149,** 385 (1983).
6. H. Yamazaki, *Anal. Chim. Acta* **113,** 131 (1980).
7. L. Chuecas and J. P. Riley, *Anal. Acta* **35,** 240 (1966).
8. C. L. Chakrabarti, *Progress in Analytical Atomic Spectroscopy* (Pergamon Press, 1979), Vol. 1.