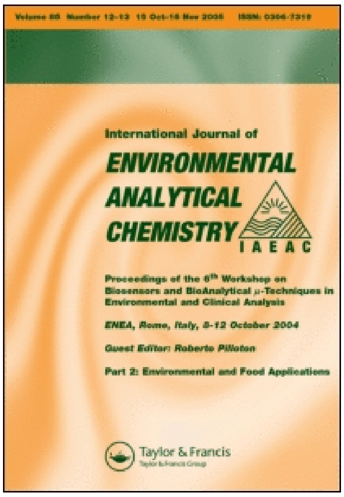

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Determination of Chromium in Environmental and Biological Samples by Atomic Absorption Spectroscopy: A Review

R. Rubio[a]; A. Sahuquillo[a]; G. Rauret[a]; Ph. Quevauviller[b]
[a] Department of Analytical Chemistry, University of Barcelona, Barcelona, Spain [b] Commission of the European Communities, Community Bureau of Reference (BCR), Directorate-General for Science, Research and Development, Brussels

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DETERMINATION OF CHROMIUM IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES BY ATOMIC ABSORPTION SPECTROSCOPY: A REVIEW

R. RUBIO, A. SAHUQUILLO and G. RAURET

Department of Analytical Chemistry, University of Barcelona,
Avd. Diagonal 647, E-08028 Barcelona, Spain.

Ph. QUEVAUVILLER

Commission of the European Communities, Community Bureau of Reference (BCR),
Directorate-General for Science, Research and Development,
Rue de la Loi 200, B-1049 Brussels.

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The technique most widely used for chromium determination in biological and environmental samples is atomic absorption spectrometry with flame (FAAS) or graphite furnace (GFAAS). In this regard, there are many articles in the literature dealing with the effect of the interferences upon chromium solutions of different oxidation state. These effects are not well established and the results are contradictory.

With the aim of joining all this information, we review the state of the art in chromium determination with AAS in environmental and biological samples. The first part of the paper is related with the different sample pretreatment methods proposed for natural and seawaters, sediments, soils, plant materials, biological materials, sewage sludges and urban particulate matter. The second part deals with the instrumental parameters and interference effects which affect chromium measurements by FAAS and GFAAS. The last part presents different certified reference materials available for the quality control in Cr determinations in the environment.

KEY WORDS: Chromium determination, FAAS, GFAAS, environmental samples, biological samples, interferences, certified reference materials.

INTRODUCTION

During the last decades chromium has deserved a considerable number of publications because of its importance not only as an essential element in living organisms but also due to its increasing accumulation in the environment from industrial inputs.

Chromium shows different levels of toxicity depending on its oxidation state, thus the hexavalent form is highly toxic in comparison with the trivalent form. Consequently, the determination of both chemical species in environmental and biological samples is a matter of interest.

In most samples chromium is present at low concentrations and so sensitive techniques must be used for determination, among which the most widely used is atomic absorption spectrometry (AAS), with flame or graphite furnace.

When chromium is to be determined in complex materials a solubilization treatment with different reagents must be used and an enhancement or a depression in the absorbance signal can be observed, which may be attributed to the presence of major components in the sample or to the addition of acids or organic compounds to the final solution. A large number of studies are reported in the literature about interfering effects in chromium determination by AAS. However, the problem is far to be solved.

This paper presents an evaluation of the state of the art in chromium determination by AAS based on the scientific literature.

The sources of error in any analytical determination can be originated from two well differentiated aspects: First, the initial treatment to solubilize the different chromium species and storage conditions of the sample, and second, the measuring step. Another source of error may be due to the lack of quality control practices in the laboratories. For this reason this paper has been divided into three parts, the first related with the sample pretreatment, the second with the final measurement and the third concerning certified reference materials.

The first part is subdivided into several sections on the different kinds of samples which are involved in environmental and biological studies and the second part also in sections according to the different methods used in AAS and the different parameters involved in the final measurement. In this part, a separate section is included for solid samples.

The last part refers to the certified materials available for the quality control of Cr determination in the environment.

SAMPLE PRETREATMENT AND STORAGE CONDITIONS

Natural waters

Cr(VI) is scarcely present in surface aquatic systems since this element occurs mainly in particulate form or remains in different physico-chemical forms in the sediments. A mean value of 1–2 $\mu g\ l^{-1}$ of hexavalent chromium may be found in surface waters[1], depending on the pollution level and to a lesser extent on the geochemical origin of the water.

Hexavalent chromium can be easily reduced to the trivalent state in polluted waters from anoxic environments.

To determine chromium in water samples it might be necessary to apply preconcentration techniques, such as volatilization, liquid–liquid extraction, sorption, ion exchange chromatography or precipitation[2]. The preconcentration techniques most frequently described are ionic exchange and chelate extraction.

Using ionic exchange, chromium is previously oxidized to chromate and then retained in an anionic column. Sodium carbonate is used as eluent[3].

For solvent extraction, chelating agents such as ammonium tetramethylenedithiocarbamate in 4-methylpentan-2-one (ATDC-MIBK)[2], as well as APDC and different organic solvents[4] are used.

Bone[5] has described a method for the determination of total chromium in effluents and natural waters, oxidizing the sample with Ce(IV) and using ammonium pyrrolidine dithiocarbamate/diisobutyl ketone (APDC-DIBK) as the extracting system. When samples contain more than 3 mg of Fe, the use of NaDDC-DIBK is recommended.

Subramanian[6] has proposed a method to determine Cr(VI), selectively, and also Cr(III) and Cr(VI) simultaneously based on the extraction in MIBK of the chelate formed with APDC. The extraction can be performed selectively by adjusting the pH.

Thompson[7] proposed a preconcentration method based on evaporation whereas Mizuike[3] used coprecipitation adding cadmium or cobalt pyrrolidine dithiocarbamates (CdPDC or CoPDC) together with indium hydroxide to produce simultaneous coprecipitation of Cr(III), Cu, Mn(II), Ni and Pb.

Arpadjan[8] proposed the elimination of Cr(III) by volatilization in the combustion step of the GFAAS by adding trifluoroacetylketone, tetramethylammonium hydroxide, methyl alcohol and sodium acetate solution.

Sturgeon[9] has reviewed storage conditions of natural waters for trace metal determination and concluded that the samples at a pH 1.5 in polyethylene bottles, may be kept for six months without decay.

Graphite furnace atomic absorption spectrometry (GFAAS) is generally used for the measurement of chromium in natural waters but flame atomic absorption spectrometry (FAAS) is also used in some cases.

Sea water

Chromium mainly occurs in hexavalent form in sea water, as can be deduced from thermodynamic calculations. However, many researchers have found that a substantial proportion of chromium exists as Cr(III) (2–50% of total inorganic chromium). This suggests a possible reduction of Cr(VI) to Cr(III) in the ocean. However, the overall distribution of chromium species has not yet been determined accurately[10].

Reported concentrations of chromium in open ocean waters range from 0.07 to 0.96 $\mu g\,l^{-1}$ [11]. Because of the interference by the sodium chloride matrix, and because of the low concentration of chromium it must first be separated and concentrated from the sea water sample.

The concentration of Cr(III) is generally much lower than that of Cr(VI), therefore, a selective method for Cr(III) preconcentration is necessary.

For removal of trace metals from sea water, preconcentration based on chelate extraction was suitable for GFAAS determinations but not for the less sensitive technique, FAAS. Chelating resins were also widely used because they allowed much higher concentration factors to be attained[12].

Isshiki[10] described a method for the selective collection of Cr(III) at nanomole level, using an adsorption chromatographic separation of the complex formed with quinolin-8-ol with methanol-HCl as mobile phase. The eluted complex was mineralized with an acid mixture and chromium is determined by GFAAS. Cr(VI) was determined by a similar method after reduction to Cr(III) with hydroxylamine.

Nakashima[13] described a method for the preconcentration of Cr(III) and Cr(VI) based on its reductive precipitation with sodium tetrahydroborate at a pH 8–9, and with addition of Fe and Pd. Then, the precipitate obtained was dissolved in an acidic mixture and determined by AAS.

To determine total dissolved chromium, Willie[11], has proposed the use of a column packed with diphenylcarbazide immobilized in silica using a previous reduction step to Cr(III) with SO_2. After elution with diluted HNO_3 the chromium was determined by GFAAS.

In conclusion, acidic mixtures are the most frequent final solutions to be measured by AAS when sea water is analysed.

Sediments, soils and geological materials

Sediments are a potential source of many of the chemical compounds dissolved in waters, therefore the determination of their metal contents deserves particular interest.

In general, processes developed for siliceous rocks are also applied to sediments. One of these methods was proposed by Purushottam[14]. The sample was digested with concentrated HNO_3 and 40% (v/v) HF and the residue was treated with aqua regia, adding ammonium bifluoride and sodium sulphate as interference supressors.

Warren[15] performed silicate rock digestion with triacidic mixtures such as concentrated HNO_3, $HClO_4$ and HF. After cooling, hydrochloric acid (1 + 1) and H_3BO_3 were added to ensure the complete dissolution of any fluoride precipitation formed.

Another procedure for treating geological materials[16] was based on an acidic digestion carrying out the elimination of the interferences by means of extractions or complexations. Sample digestions were performed with mixtures of HF, HNO_3, $HClO_4$ and H_2SO_4. The subsequent extraction of the residue with *n*-butylacetate allowed the elimination of interfering Fe(III) in the organic layer as a chlorocomplex, and the addition of EDTA in the aqueous layer eliminated the Mn(II) interference. After addition of NaDDC-MIBK, chromium was determined in the organic phase by FAAS.

The methods especially designed for sediment treatments undergo attack by acidic digestions or to a lesser extent by fusions. Agemian and Breder[17,18] described methods of treatment with triacidic mixtures (HNO_3, $HClO_4$, HF) as well as binary acidic mixtures in different ratios.

Farmer[19] and Bettinelli[20] proposed methods also based on acidic digestions. The former described a method that used aqua regia and HF, followed by the addition of a saturated solution of H_3BO_3, whereas Bettinelli treated the sample with a mixture of HNO_3, $HClO_4$ and HF. He also described a method of fusion, treating the sample with lithium tetraborate.

Another method of acidic digestion for sediments was proposed by Sturgeon[21] who used a two-step procedure. The first was carried out in a mixture of HCl, HNO_3 and HF and the second with HNO_3 and $HClO_4$.

With respect to soil samples, the treatment proposed by Ajlec[22] was different for total and exchangeable chromium. For total chromium the dried sample was digested with a mixture of HNO_3–$HClO_4$–HF whereas for exchangeable chromium EDTA was added to the sample and the extract was ashed. The residue was dissolved in HNO_3 (1 + 1). After digestion Cr(III) was oxidized to Cr(VI) with $KMnO_4$ and it is extracted with MIBK as $HCrO_3Cl$ after the addition of HCl. This extraction was selective at 4°C. Chromium in the organic phase was determined by FAAS.

In general, after a strong treatment to solubilize trace metals, the acidic mixture was evaporated and hydrochloric or nitric solutions were added. The chromium content in these final solutions were mainly determined by GFAAS or less frequently with FAAS.

Plant materials

Chromium is widely distributed in plant materials at trace levels. The treatment of rye samples described by Ihnat[23], consisted in ashing the samples overnight and dissolving the residue in HCl.

The method described by Ajlec[22] for tomato leaves, involved two possible ashing procedures, dry and wet. For the dry ashing, the sample was heated to 773 K for 12 hours and the ashes were treated with a mixture of HF and H_2SO_4 in order to eliminate silica and to prevent chromium losses by absorption. For wet ashing, the sample was digested with a mixture of $HClO_4$ and HNO_3 and kept overnight. An extraction with HCl-MIBK was performed, after an oxidation of Cr(III) to Cr(VI) with $(NH_4)_2S_2O_8$.

Acidic mixtures or the organic layer were the final solutions to be measured for these materials.

Biological materials

The determination of chromium in biological fluids is difficult because of the low levels that must be determined, down to the 0.1 $ng\,g^{-1}$ range[24].

For this reason almost all the papers related to these samples used a graphite furnace for chromium determination. The graphite tube atomizer has other advantages such as the small sample volume required and the possibility of analyzing samples containing organic matter without pretreatment.

The biological samples most commonly analyzed are urine samples, blood and plasma, human milk and tissues.

The preservation of the samples is usually done at low temperatures in acidic media or with preservative reagents.

Generally, the procedures used for biological material treatment are based on acidic digestion. Schramel[25], used a digestion method with concentrated sulphuric acid and 50% (v/v) hydrogen peroxide for the destruction of the biological matrices.

In the literature specific procedures for different kinds of samples were described especially for urine, urine and blood, urine and plasma, urine and human milk, serum and tissues.

For urine sample treatment, a method based on oxygen plasma ashing of the sample was described by Guthrie, Veillon and Wolf[26,27]. Complete decomposition of the samples was achieved with H_2O_2 50% (v/v) and the final ashes were dissolved in diluted HCl and analyzed. In addition, Dube[28] and Veillon[24] proposed direct determination of urine samples.

For urine and blood samples, Feldman[29] described two types of decomposition: for dry ashing, the samples were treated during 4–5 hours at 550°C; for wet decomposition, the sample was digested with a mixture of HNO_3–H_2SO_4–$HClO_4$ followed by the addition of $KMnO_4$ in order to oxidize chromium to the hexavalent state, which was extracted with MIBK after addition of HCl. The organic phase was analyzed by AAS.

Hinderberger[30] described two methods of digestion applicable to blood and urine samples. For blood samples, a treatment with HNO_3 at 100°C was carried out. For urine samples, a nitric acid digestion was performed. For both samples chromium was determined in the acidic medium by GFAAS.

For urine and plasma samples, Davidson[31] described a sample treatment using $HClO_4$ in especially designed vials, and evaporation to dryness. The final residue was dissolved in HCl.

For urine and human milk samples, Kumpulainen[32] described a drying method for urine samples in a vacuum oven and for human milk in a hot plate. The author proposed two ashing procedures: by dry ashing, where the samples were heated to 500°C in a covered aluminium container. The final residue is dissolved in diluted HCl. When oxygen plasma ashing is used a two-step procedure is performed with the addition of H_2O_2. The residue is treated with diluted HCl.

To analyse Cr in human serum, Veillon[24,33] lyophilized and dry-ashed the samples adding magnesium nitrate as an ashing aid. The residue obtained was dissolved in diluted HCl.

Lewis[34] also used a temperature-programmed dry-ashing method up to 480°C, for blood serum samples. The ashes were dissolved in HNO_3, adding magnesium nitrate as ashing/modifier.

For tissue samples, decomposition treatments are mainly based on acidic digestion. Ramos[35] performed sample digestion with a mixture of H_2SO_4–HNO_3. Veillon[24] ashed samples at 350°C for 24–48 hours. Then a small amount of HNO_3 and H_2O_2 was added to the residue and samples were heated. The residue was dissolved in dilute HCl. Finally, Betts[36] performed sample digestion in HNO_3. The final residue was dissolved with HNO_3 1% (v/v).

For food samples, Jackson[37] described a similar method as for biological material. Organic material was decomposed by a wet-digestion method with HNO_3 and H_2SO_4. A sequential extraction was developed to determine Co, Ag and Cr. Diethylammonium diethyldithiocarbamate (DDDC) was used to complex Ag and Co, and pentane-2,4-dione to complex chromium. Na_2SO_3 was added to improve Cr(III) extraction, being 4-methylpentan-2-one the organic extractant. The analysis was performed on the organic phase.

Urban particulate matter; welding fumes

The main sources of chromium pollution in the atmosphere are traffic, the combustion of coal and the emissions from metallurgical industries.

The sample collection is performed by pumping air through membrane filters. As the respirable particles are very fine, the mesh of the filters used should be very small even though this reduces the air flow.

The analysis of urban particulate matter could be performed on solid matter or after filter solubilization. To analyse some trace metals, Schlemmer[38] introduced approximately 1 mg of solid sample into the graphite furnace and optimized the atomizing temperature according to matrix characteristics and element volatility. Ramos[39] used filter digests. The sample treatment consisted of acidic digestion with HNO_3 and $HClO_4$ and heating until near dryness. The final residue was dissolved in diluted HNO_3.

The procedures proposed by NIOSH[40] consisted of a wet ashing of the sample using hydrochloric and nitric acids to destroy the filter and organic materials. Treatment with HCl allowed the solubilization of any chromium metal which may be present. The final residue was dissolved in concentrated HNO_3.

Another important source of pollutants are welding fumes. In this case, Brescianini[41] described an alkali treatment using Na_2CO_3 3% (w/w) and NaOH 2% (w/w) in order to achieve complete Cr(VI) dissolution. The alkali extract was therefore analysed by GFAAS.

Sewage sludges

The methods described to determine chromium in sewage sludges are based on acidic digestions. The method described by Thompson[7] for natural waters is also applied to sewage sludges by the same author. Inhat[23] performed dried sample digestion with aqua regia. Thompson[42] also described different kinds of digestions for sewage sludges. The author, after assaying HNO_3, H_2SO_4 and H_2O_2 in different ratios, recommended nitric acid digestion.

Carrondo[43] used two digestion procedures, a H_2SO_4–HNO_3 method and a HNO_3–H_2O_2 method for the analysis of sewage effluents and sewage sludges. Afterwards, the organic matter was decomposed by ashing using an ethanolic solution of magnesium nitrate. No significant differences were observed when two digestion procedures were applied in chromium determination.

Conclusions

From the reported literature it can be concluded that most of the resulting final matrices consist of acidic solutions or, to a lesser extent, the final solution is a carbonate-hydroxide extract.

When chelate extractions are applied to isolate chromium species the organic final extracts are mainly MIBK or DIBK.

The different sample pretreatments of environmental and biological samples are summarized in Table 1.

Table 1 Sample pretreatment for Cr determination.

Sample	*Pretreatment procedure*	*Reagents*	*References*
Natural waters	Ionic exchange	Anionic column	(3)
	Chelates extraction	ATDC-MIBK	(2, 3)
		APDC-DIBK	(5)
		APDC-MIBK	(6)
	Evaporization	Al-H_2O_2	(7)
	Coprecipitation	CdPDC or CoPDC	(3)
	Selective volatilization	Trifluoroacetyl ketone	(8)
		Tetramethylammonium hydroxide	
		Methyl alcohol	
		Sodium acetate	
Sea water	Chelate resin	Diphenylcarbazide	(11)
	Adsorption chromatography	Quinolin-8-ol	(10)
	Reductive precipitation	Sodium tetrahydroborate	(13)
Siliceous material	Acidic digestion	HNO_3–HF	(14)
		HNO_3–HF–$HClO_4$ (+H_3BO_3)	(15)
	Acidic digestion and extractions	HF–HNO_3–$HClO_4$–H_2SO_4 (NaDDC-MIBK)	(16)
Sediments	Acidic digestion	HNO_3–$HClO_4$–HF	(17, 18, 20, 21)
		Aqua regia-HF	(19)
	Fusion	Lithium tetraborate	(20)
Soils	Acidic digestion	HNO_3–$HClO_4$–HF	(22)
	Ashing	773 K	(22)
Plant material	Ashing	—	(23)
	Wet ashing	H_2SO_4–HF	(22)
		$HClO_4$–HNO_3	(22)
Biological material	Acid digestion (general)	H_2SO_4–H_2O_2	(25)
Urine	Plasma ashing	H_2O_2 (50%)	(26, 27, 32)
	No treatment		(28)
	Kjeldahl		(30)
Urine and blood	Dry ashing	550°C	(29)
	Wet ashing	HNO_3–H_2SO_4–$HClO_4$	(29)
		$KMnO_4$	
		HNO_3	(30)
Urine and plasma	Wet ashing	$HClO_4$–H_2O_2	(31)
Urine and milk	Dry ashing	H_2O_2	(32)
Human serum	Lyophilization		(24, 33)
	Dry ashing	$MgNO_3$	(34)
Tissues	Acidic digestion	H_2SO_4–HNO_3	(35)
		HNO_3	(36)
	Dry ashing		(24)
Foodstuff	Acidic digestion and extraction	HNO_3–H_2SO_4	(37)
		pentadione+MIBK	
		Na_2SO_3	
Urban particulate matter	No pretreatment		(38)
	Acidic digestion	HNO_3–$HClO_4$	(39)
	Wet ashing	HCl–HNO_3	(40)
Sewage sludges	Acidic digestions	HNO_3	(42)
		H_2SO_4–HNO_3	(43)

MEASUREMENT STEP

ATOMIC ABSORPTION SPECTROSCOPY WITH FLAME

There are two groups of important factors affecting the formation of neutral atoms in flames. On one hand, it is necessary to optimize the instrumental parameters such as flame stoichiometry and measuring conditions, and on the other a study on matrix interferences and release agents is required. In the literature, there are studies on these two aspects, for both air-acetylene and nitrous oxide-acetylene flames.

Air-acetylene flame

The main parameters mentioned are oxidant-fuel ratios in the flame, type of burner, height over the burner where the measurement is performed, slit-width, lamp intensity and background corrector.

In all the articles found, the measurements are performed at 357.9 nm, corresponding to the most sensitive line for chromium.

Table 2 shows the ranges of the variables found in the literature. According to this, the most important parameter seems to be the oxidant/fuel ratio in the flame. Thompson[44], Aggett[45] and Purushottam[14], observed significant differences in the behaviour of Cr(VI) and Cr(III) solutions depending on the stoichiometry of the flame, due to the chemical nature of the species formed on droplet desolvation. Although in the hotter fuel-lean air-acetylene flames depressing or enhancing effects are almost negligible, the sensitivity is too low to permit determinations of traces of Cr in some samples. A ten-fold increase in sensitivity between the fuel-lean and fuel-rich flames has been shown[14].

The composition of the flame plays an important role not only in the sensitivity but also in the behaviour of the interfering compounds, and a situation of compromise between both aspects should be achieved for each kind of samples. Broncano[46] recommended the use of a medium-rich flame, and Thompson[44] observed that in the luminous flame the absorbance depends on the age of the chromium solution.

With regard to the radiation source, it was found that the light intensity has no significant effect on the chromium absorption signal[14].

The use of background corrector is not as important in the determination by FAAS as it is in the graphite furnace mode. However, in some articles the deuterium arc was used and the application of the Zeeman effect was also described to improve the detection limits[47].

Aerosol drop size also influence the signal. Smith[48] found that condensed-phase produces a depressing effect.

Study of the interferences

Different kinds of interfering substances are described in the literature such as cationic, anionic and acidic matrices resulting from the sample digestion methods. The interfering species, the observed effects as well as the releaser agents are summarized in Table 3.

Table 2 Instrumental parameters in air-acetylene flame.

Parameter	*Range*	*Reference*
Oxidant/fuel ratio	0.77–0.96	(45)
	0.77	(51)
	slightly fuel-rich	(37)
	2.35	(14)
	0.36	(53)(54)
	verge of luminosity	(7)
	2.7–3	(56)
	3	(52)
	7	(58)
	5.45	(60)
	1.98–6	(23)
	fuel-rich	(5)(57)
Type of burner	3 slot burner	(46)(37)(58)(15)
	High-solids air-acetylene burner	(7)(44)
	10 cm slot burner head	(54)(53)(51)(14)(58)(60)(46)(23)
Burner height (mm)	Dinitrogen oxide-acetylene burner	(45)(50)
	14	(52)
	4–14	(56)
	2–10	(45)
	0–20	(50)
	3.5–4	(44)(42)(7)(5)
	6	(54)
	8	(49)
	7.5–10.5	(53)
	10	(55)
	5	(6)
	5.5–15.5	(46)
	3–10	(23)
	1.5–3.7	(22)
Slit-width (nm)	0.5	(7)(44)(42)
	0.2	(42)(46)(56)(52)
	0.1	(54)(14)
	0.15	(55)
	0.33	(23)
	0.03–0.05	(57)
Lamp intensity (mA)	10	(45)(55)(14)
	12	(54)(57)
	5	(56)(23)(47)
	8	(22)(52)
Background corrector	357.3 nm (Pb)	(7)
	Automatic	(42)
	Deuterium arc	(37)(53)
	352 nm	(23)

Table 3 Interferences in air-acetylene flame.

Interferent	*Observed effect*	*Releaser agents*
Upon Cr(VI)		
Na, K, Li	Depressing (50, 49)	N_2O-C_2H_2 flame (49) NH_4HF_2 (14) NH_4Cl or Na_2SO_4 (51)
Ba	Enhancing (49)	$NH_4HF_2 + Na_2SO_4$ (14)
	Depressing (51)	Na_2SO_4 (51)
Mg	Enhancing (49)	$NH_4HF_2 + Na_2SO_4$ (14)
	Depressing (51)	NH_4Cl (51)
Ca	Enhancing (49)	NH_4Cl (51) NH_4HF_2 (14)
Sr	Depressing (49)	N_2O-C_2H_2 flame (49)
Cu	Enhancing (49)	$NH_4HF_2 + Na_2SO_4$ (14)
	Depressing (51)	Na_2SO_4 (51)
Co	Enhancing (49)	NH_4HF_2 (14)
	Depressing (51)	Na_2SO_4 (51)
Fe	Enhancing (49)	NH_4Cl or Na_2SO_4 (51)
	Depressing (51, 52)	NH_4HF_2 (14)
Zn, Sn	Depressing (49)	NH_4HF_2 (14)
Ni	Depressing (51, 52)	$NH_4HF_2 + Na_2SO_4$ (14)
Ti, Mo, Mn, Ag, Hg	Depressing (51)	$NH_4HF_2 + Na_2SO_4$ (14)
Al	Enhancing (49)	NH_4HF_2 (14)
	Depressing (52)	Na_2SO_4 (51)
W, Ce	Enhancing (51)	NH_4HF_2 (14) Na_2SO_4 (51)
Upon Cr(III)		
Fe	Depressing (49, 53, 54)	NH_4HF_2 (51) NH_4ClO_4 (7, 42) SSA (54)
Mn, Ni	Depressing (49)	$NH_4HF_2 + Na_2SO_4$ (14) SSA-boric acid (54)
Zn, La	Enhancing (53)	NH_4HF_2 (14)
Mo, Rh	Depressing (55)	NH_4HF_2 (14)
I^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}	Depressing (54)	Boric acid (54) SSA-KCN (54) NH_4ClO_4 (7)
Citrate	Slight depressing (56)	—
Upon both Cr(VI) and Cr(III) solutions		
H_3PO_4, H_2SO_4, $HClO_4$	Depressing (51, 14)	Na_2SO_4 (51) NH_4HF_2 (14)
HCl	Depressing (52)	NH_4Cl (51)
	No effect (51, 14)	NH_4HF_2 (14)
HNO_3	No effect (51, 14, 52)	NH_4Cl (51) NH_4HF_2 (14)
CH_3COOH	No effect (52)	—

Cationic interferences in Cr(VI) solutions. For Cr(VI) solutions, the presence of cations as well as the use of interference supressors, produce different effects.

With regard to alkaline metals, Yanagisawa[49] and Aggett[50] observed a depressing effect of Na, K and Li in acidic media upon Cr(VI) primary standard solutions and chromium trioxide solutions, respectively.

For alkaline earth metals, the effects observed by the authors are different. Yanagisawa[49] observed enhancing effects with Ba, Mg, Ca added as chlorides and depressing effects with Sr chloride, whereas Hurlbut[51], described depressing effects with Mg and Ba when they were added as nitrates, in a higher Cr/interference ratio than in the Yanagisawa studies[49].

According to Yanagisawa[49], Al produces enhancing effects whereas Diaz[52] found depressing effects and Hurlbut[51] described a different behaviour of Al depending on the oxidant/fuel ratio in the flame.

With transition metals, reports are also contradictory. Yanagisawa[49], described enhancing effects for Cu, Co and Fe and depressing effects for Zn and Sn, whereas Hurlbut[51] and Diaz[52] observed depressing effects for Ni and Fe. Hurlbut[51] also described depressing effects with Ti, Mo, Mn, Co, Cu, Ag and also Hg. In addition, W and Ce were shown to produce enhancing effects[51].

Removal of cationic interferences. Different ways of removing cationic interferences are described. Yanagisawa[49] eliminated the interferences found in a air-acetylene flame by using a nitrous oxide-acetylene flame.

Na_2SO_4, Na_2SO_3, K_2SO_4, $K_2S_2O_8$ and NH_4Cl were investigated as supressor agents, but Hurlbut[51] found that the addition of Na_2SO_4 to the samples effectively eliminated the interferences due to high cation concentrations. According to Purushottam[14] ammonium bifluoride eliminates the interfering effects caused by most of Fe, Al, Ca, Mg, Co(II), Ni, Mn(II), Mo(VI), W(VI), Hg(II), As(III), Ba and Cd cations.

A quantitative chemical separation process was described by Hannaker[16] to eliminate Fe(III) and Mn(II) interferences during a solvent extraction procedure to determine Cr in geological materials. Fe(III) was removed from the aqueous phase by extracting the chlorocomplex with *n*-butylacetate. In the aqueous phase, Mn(II) is masked with EDTA and chromium was determined in the organic phase after an extraction with the NaDDC-MIBK system. Bone[5] agreed with Hannaker[16] in the use of NaDDC as extractant instead of APDC in a procedure for total chromium determination in water samples, because NaDDC is less interfered by Fe.

Cationic interferences in Cr(III) solutions. In general, all cations mentioned in the literature, produce the same effect in both Cr(VI) and Cr(III) solutions but there are differences.

Yanagisawa[49], Jedrzejewska[53] and Abdallah[54], observed a depressing effect for Cr(III) solutions in the presence of Fe in acidic media, an effect which increases with higher Fe concentrations.

Furthermore, elements such as Mn and Ni, which do not give significant effects for Cr(VI), show depressing effects for Cr(III), according to Yanagisawa[49].

Zr and La enhance the absorption signal when a fuel-rich flame is used, was was shown in a study performed by Jedrzejewska[53], whereas Abdallah[55] described a depressing effect caused by Mo and Rh in phosphoric acid media.

Removal of cationic interferences. Different ways were proposed to remove interferences, such as the modification of any instrumental parameter or the use of a release agent.

Among modifications of instrumental parameters, Abdallah[54] found that the Fe or Ni effect were highly dependent on the region of the flame where the observation was carried out and that at a determined height of the flame this effect disappeared.

As realease agents, Purushottam[14] used a mixture of NH_4HF_2 and Na_2SO_4 because ammonium bifluoride was not effective enough for Cr(III) solutions. Thompson[7,42] assayed NH_4ClO_4 and NH_4Cl, and NH_4ClO_4 gives the best results with Ca, Na, Mg and Fe interferences in natural waters and sewage effluent samples. The addition of lanthanum chloride as interference supressor at high concentrations, did not improve the absorption signal for chromium in sewage sludge samples, although when nitrous oxide-acetylene flame was used the results obtained were much better. Abdallah[54] proposed boric acid and sulphosalicylic acid as release agents. Both species effectively remove Al, Ca, Sr, Fe(III), Ni, Cu, Pb, Mn and In interferences.

It can be concluded that most cations interfere in chromium measurements but their effects are of different extent, depending on the oxidation state of chromium, the flame stoichiometry, and the sample matrix. Different ways may be used to remove these interferences.

Anionic interferences. Few anionic interferences are described in the literature and they are only referred to Cr(III) solutions.

I^-, NO_3^-, NO_2^- , PO_4^{3-} and SO_4^{2-} were described by Abdallah[54] as depressors of Cr(III) absorption signal and Diaz[56] found a slight depressing effect produced by ammonium dibasic citrate which can be eliminated by modifying the burner height.

Removal of anionic interferences. As release agents, Abdallah[54] showed the effectiveness of boric acid, sulphosalicylic acid (SSA) and KCN in the recovery of chromium at 1.10^{-3} mol l^{-1} level, and Thompson[7] found that NH_4ClO_4 in HCl gave good results even if Ca and Mg were present in the solution.

Interferences of acids. The effects of acidic interferences described are the same for both Cr(VI) and Cr(III) solutions.

H_3PO_4, H_2SO_4, $HClO_4$ act as signal depressors upon solutions of chromium while HCl and HNO_3 do not interfere[14,51]. Diaz[52] found that HCl produces a depressing effect in the overall range of concentrations studied, and HNO_3 and CH_3COOH do not rinse to significant interferences.

Among the usual release agents to remove acidic interferences, Hurlbut[51] found that NH_4Cl is the most effective at low and high acidic concentrations. Ammonium bifluoride or a mixture with sodium sulphate was used by Purushottam[14].

Table 4 Recoveries found in air-acetylene flame.

Ref.	*Cr: interference*	*Metals*	*Realeyer agent*	*Recov.*
(51)	1:100 (10 $\mu g\ g^{-1}$ of Cr)	Mo, Mn, Fe, Co Ni, Cu, Al, Cd	Na_2SO_4 (1%)	100
(14)	1:100 (10 $\mu g\ g^{-1}$ of Cr)	Fe, Mn, Al, Ca Mg, Co, Ni	NH_4HF_2 (1%)	99
(7)	1:50–1:500 (1 $\mu g\ g^{-1}$ of Cr)	Ca, Mg, detergent, SO_4^{2-}, Zn, Mn, NH_4^+, NO_3^-, SiO_2	NH_4ClO_4 (2%)	96–101
(54)	200 $\mu g\ g^{-1}$ interf. in a 1.10^{-3} M solution Cr(III)	PO_4^{3-}, NO_3^-, EDTA, SO_4^{2-}, ClO_4^-, Al, Ca, Sr, Fe, Ni, Cd	Boric acid SSA KCN	98–100 95–100 99–105*

* Except for cations because of metalic cyanide precipitation.

Quality parameters in air-acetylene flame

Tables 4 and 5 review the values of quality parameters, i.e. accuracy, precision and detection limits for air-acetylene flame. The information is obtained from standard solutions and real samples such as natural waters and siliceous materials.

In general, the interference suppressors are effective and a good accuracy in the measure is claimed to be achieved.

Nitrous oxide-acetylene flame

It is well known that many sources of interferences which are present in an air-acetylene flame are eliminated by the use of the nitrous oxide-acetylene flame.

The interfering effects in this flame depend upon flame richness and may be eliminated by chosing the optimum fuel/oxidant ratio, although the dependence is not as important as in the air-acetylene flame.

Most of the reports found are mainly based on the comparison of the two flames in studies concerning cationic, anionic and acidic interference as well as optimization flame conditions.

Table 5 Detection limits in air-acetylene flame.

Material analysed	*Ref.*	*Replicates*	*D.L.* *($\mu g\ g^{-1}$)*	*RSD* *(%)*
Standard $K_2Cr_2O_7$	(57)	—	0.4	—
Silicic material	(14)	—	—	1.3–8
Rock sample	(15)	6	—	8
Natural waters	(7)	2	0.0043	2.2–7.15
Standard solutions	(5)	6	—	2.2–6.9
Standard solutions	(47)	—	0.004	—
Foodstuff	(37)	—	—	4–28
Sewage sludges	(42)	—	—	1.6–16.6

Table 6 Instrumental parameters in N_2O–C_2H_2 flame.

Parameter	*Range*	*References*
Oxidant/fuel ratio	1.7–2.1	(58)
	2.3	(60)
	1.9	(46)
	1.8–2.7	(23)
Burner height (mm)	1–5	(58)
	4	(60)
	4.5–14.5	(46)
	2–24	(23)
	4.8	(22)
Slit-width (nm)	0.2	(46)
	0.33	(23)
	0.1	(22)
Burner type	10 cm 3-slot	(58)
	5 cm burner head	(60)(46)(58)
	6 cm burner head	(23)
Lamp intensity (mA)	5	(23)
	8	(17)
Background corrector	352 nm	(23)

The instrumental parameter values found in the literature for N_2O–C_2H_2 flame model are shown in Table 6. All measurements are performed at the wavelength of 357.9 nm.

The oxidant/fuel ratio is one of the most important parameters in the flame, and the three stoichiometries: lean, medium and rich fuel were investigated. Broncano[46], recommended the use of a lean nitrous oxide-acetylene flame. Smith[48], found that condensed-phase interference gives signal enhancements in nitrous oxide-acetylene flame.

Study of the interferences

The main interferences described in the literature are referred to the acidic matrix and cations, mainly in Cr(VI) solutions. The interfering compounds, the observed effect as well as the realeaser agents, are given in Table 7.

Table 7 Interferences in N_2O–C_2H_2 flame.

Interferent	*Observed effect*	*Releaser agents*
Fe	Slightly depressing (22) No effect (48)	Not described
Ti	Depressing (48)	Not described
Al, Ca, Mg	No effect (22)	Not described
HNO_3, HCl	Negligible effect (23, 58)	Not described
$HClO_4$, H_2SO_4	Depressing (58)	Not described
H_3PO_4	Variable depending on burner position	Not described

Cationic interferences. Cationic interferences are easier to overcome in nitrous oxide-acetylene than in air-acetylene flame.

Nitrous oxide-acetylene flame reduces[22] or even supresses[48] the depressing effect of Fe observed in air-acetylene flame. Smith[48] found that Ti is the only element which produces a significant interference on the Cr absorption signal when using a fuel-rich nitrous oxide-acetylene flame.

Severe signal depressions observed in the air-acetylene flame for cation mixtures with alkali and transition metals in HNO_3 and H_3PO_4 media, are completely eliminated by using the nitrous oxide-acetylene flame[23]. Ajlec[22] did not find that Al, Ca and Mg interfere when N_2O-C_2H_2 flame is used.

Interference of acids. Nitrous oxide-acetylene flame easily overcomes the acidic effects on chromium absorbance.

HNO_3 and HCl produce almost negligible effects in the lean nitrous oxide-acetylene flame, as was observed by Barnett[58] and Ihnat[23]. $HClO_4$ and H_2SO_4 were described as depressors by Barnett[58]. This author also found that the effect of H_3PO_4 depends on the burner position: in the normal position it gives enhancing effects whereas it gives depressing effects in the perpendicular position. On the other hand, Inhat[23] found that H_3PO_4 effects are hardly significant in the lean nitrous oxide-acetylene flame.

Conclusion

In the determination of chromium by AAS, the N_2O–C_2H_2 flame is not subjected to interferences or at least they are easier to remove than in an air-acetylene flame, and in most cases the addition of a supressor agent is not necessary.

Furthermore, the N_2O-C_2H_2 flame does not show different sensitivity for Cr(III) and Cr(VI) compounds in contrast to air-acetylene flame.

Quality parameters

The data for N_2O-C_2H_2 flame are not as abundant as for air-acetylene flame, and they refer to the precision and accuracy of the determinations. Table 8 shows the reported detection limits and recoveries.

With regards to precision, coefficients of variation were presented only in one

Table 8 Quality parameters in N_2O–C_2H_2 flame.

Method	*Material analysed*	*D.L.*	*Recov. (%)*	*Ref.*
Acidic digestion	Sewage sludges	—	101–107	(23)
Acidic digestion ($HClO_4$, HF)	Plant material	0.02 ($\mu g\,g^{-1}$)	—	(22)
According to standard methods	Water	6.2	100	(59)

article. The short term and long term precisions ranged, respectively, between 2.6–3.4% and 12.3–12.9%[59].

The detection limit values are of the same order of magnitude for the N_2O–C_2H_2 flame than for the air-acetylene flame.

Air-hydrogen flame

Cresser[60] studied the variation of Cr(III) and Cr(VI) absorption signals as a function of pH in air-acetylene, air-hydrogen and nitrous oxide-acetylene flames. With air-hydrogen flame there is a pronounced depressing effect on the absorbance between 5 and 8 pH units, when Cr(VI) solutions are assayed.

GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY

Graphite furnace atomic absorption spectroscopy permits the determination of chromium at low levels, even in complex matrices, when using the Zeeman effect, background correction, platform atomization and matrix modification.

The nature of the atomizer surface is of paramount importance, because the analyte, as well as the matrix, penetrate into the graphite structure and they interact strongly. As a result, the graphite surface determines the kinetics of the reactions in heterogeneous or condensed phases[61]. The nonuniformity of chromium profiles within the graphite furnace atomizer appears to be element-dependent and affected by the chemical nature of the surface[62].

Considerable disagreement exists in the published data concerning the volatility of chromium during thermal pretreatment of various sample solutions in the graphite tube.

With respect to atomization mechanisms, Genç[63] proposed a thermal dissociation of the metal oxide and reduction of the oxide by carbon into the furnace, followed by vaporisation of the elemental metal. Chakrabarti[64], estimated that both carbon reduction and the thermal decomposition of the metal oxides are spontaneous chemical reactions.

Wendl[65] and Matousek[66], agreed that the formation of refractory metallic carbides is responsible for incomplete chromium release, while Arpadjan[67] did not support the hypothesis of strong carbide formation.

From the experimental point of view different types of furnaces have been described in the literature: uncoated tubes, pyrolytically-coated tubes and tungsten and zirconium coated tubes. For each one, the programs, modifiers and background correctors used will be described in the following paragraphs.

Uncoated tubes

The instrumental parameters mentioned in the literature are shown in Table 9. All measurements were performed at the wavelength of 357.9 nm. The different furnace programs depending on the sample solution are shown in Table 10.

Table 9 Instrumental parameters in uncoated tubes.

Parameter	*Value*	*References*
Slit-width (nm)	0.2	(31)(69)(43)
	0.4	(26)
	0.7	(19)(35)(6)
Sample volume (μl)	5	(69)
	10	(6)(70)(25)
	20	(19)(35)(43)
	30	(26)
	50	(31)(43)
Sample introduction	Micropipettes	(31)(26)(69)(35)(43)
	Automatic sampler	(19)(6)(10)
Inert gas	N_2	(31)
	N_2 interrupted atom.	(26)
	Ar	(43)(35)
	Ar interrupted atom.	(6)(19)(70)
Lamp intensity (mA)	15	(31)
	10	(35)
	25	(6)
Background corrector	Deuterium arc	(26)(19)(35)(25)(43)
	Not necessary	(6)

The optimization of instrumental parameters and temperature programs is very important. For example, Guthrie[26] found that the background signal increases with increasing injected sample volume and so does apparent chromium.

The range of furnace temperatures in the different steps are: drying, 100–120°C; ashing, 900–1350°C; atomizing, 2200–2700°C.

Study of the interferences

Cations, anions, and acids are described as major sources of interferences in chromium determinations by electrothermal AAS using uncoated tubes, with similar

Table 10 Temperature programs in uncoated tubes.

Ref.	*Drying (°C)*	*Ramp (s)*	*Hold (s)*	*Ashing (°C)*	*Ramp (s)*	*Hold (s)*	*Atomizing (°C)*	*Ramp (s)*	*Hold (s)*
(31)	100	—	100	1100	—	60	2400	—	12
(69)	110	—	30		Variable		2200	—	4
(19)	105	—	30	920	—	40	2700	—	12
(68)	—	—	—	1100	—	25	2600	—	10
(35)	120	10	15	1200	25	10	2700	1	6
(6)	—	—	—	900	30	30	2500	0	6
(26)	120	—	30	1300	—	30	2600	—	9
(25)	100	—	30	1350	—	10	2500	—	5
(70)	110	—	30	—	—	15	—	—	10
(43)	100	—	30	1100	—	30	2660	—	5

Table 11 Interferences in uncoated tubes.

Interferent	*Observed effects*	*Matrix modifiers*
Mg, Na, Al, Ca, Ti	Depressing (68)	Not described
Cl^-, I^-, CO_3^{2-}, HPO_4^{2-}, SO_4^{2-} Cl^-	No effect (31) Variable (69)	EDTA (masking) (69)
HNO_3	No effect (70) Depressing (35)	No matrix modifier described
H_2SO_4	Depressing (35)	
Humic acid	Depressing (6)	

effects for Cr(III) and Cr(VI) solutions. The interferences, their effects as well as the matrix modifiers used are shown in Table 11.

Cationic interferences. Cation effects were studied on biological samples and sediments. In general, alkali and transition metals give almost negligible effects in the resulting solutions after treatment. Schramel[25] did not find any interference in biological samples and Subramanian[6] did not observe interferences with a multielemental cationic solution in an extraction procedure of seawater samples using the APDC-MIBK system. Davidson[31] eliminated metal interferences with a double atomization process. Only Legret[68] found that Mg, Na, P, Al, Ca and Ti seriously inhibit the absorbance signal in solutions resulting from sediment attacks.

Anionic interferences. Davidson[31] found that Cl^-, I^-, CO_3^{2-}, HPO_4^{2-} and SO_4^{2-} did not affect chromium peak height when they are in high concentration levels and using a double atomization procedure. However, Matsusaki[69] detected one important interference caused by chlorides and removed this by preventing chloro-complex formation with the analyte and coexisting cations. This may be achieved by volatilizing the chloride or by conversion of the metallic chloride into oxide before atomization, or by the addition of any masking agent such as EDTA to avoid chloride coordination with the analyte.

Interferences of acids. Alder[70] found that HNO_3 does not significantly enhance or reduce the atomic absorption signals for chromium, whereas Ramos[35] showed that HNO_3 and H_2SO_4 acids cause a depression in the signal.

Subramanian[6] studied the effect of humic acid on Cr absorption in water samples and found that increasing concentrations lead to lower recovery results for chromium. Carrondo[43] did not detect any acidic interferences even in sewage sludges samples.

No matrix modifier to eliminate interference of acids was described in the literature.

Quality parameters

Results from the different methods with uncoated tubes, with respect to quality parameters are given in Table 12. Different authors obtain recovery values ranging between 94.5% and 109.9%[6,10].

Table 12 Quality parameters in uncoated tubes.

Ref.	*Replicates*	*RSD %*	*D.L.*	*Analysis*
(31)	—	1.2–2.1	2 pg	Calibration
(31)	—	5.2	—	STD addition
(19)	8–12	1	5 $\mu g\ g^{-1}$	Calibration
(35)	—	<5	0.0025 $\mu g\ g^{-1}$	Calibration
(25)	10	0.19	—	Calibration
(10)	—	—	0.025 nM	—

Pyrolytically-coated graphite tubes

The different values of the instrumental parameters found in the literature are indicated in Table 13.

Pyrolytically-coated tubes produce a 3-fold increase in sensitivity with respect to the uncoated ones, but some instrumental problems have been mentioned. These basically refer to background correction, although Nakashima[13] mentioned effects of other parameters such as slit-width.

Guthrie[26] showed that a conventional deuterium background corrector was unsuitable for chromium in urine matrices and proposed some alternatives as Zeeman effect or the use of a light with greater intensity at chromium wavelength. Wavelength-modulation was also described to overcome this problem[26,33]. In other kinds of samples, like human milk[32], this problem seemed not to be relevant.

Table 13 Instrumental parameters in pyrolytically-coated tubes.

Parameter	*Values*	*References*
Slit-width (nm)	0.2	(13)(71)
	0.4	(41)
	0.7	(32)(33)(20)(28)(72)(81)(82)
Sample volume (μl)	10	(32)(21)
	20	(32)(20)(34)
	20–40	(28)
Sample introduction	Micropipettes	(33)(34)
	Autosampler	(28)(13)(21)(82)(73)(34)
Inert gas	Ar	(33)(34)
	Ar interrupted atom.	(20)(28)(81)
Lamp intensity (mA)	10	(39)(41)
	15	(81)(72)
	20	(20)
	25	(33)(28)
Background corrector	Deuterium arc	(32)(20)(72)(73)
	Zeeman effect	(11)(28)(13)(73)(36)
	Tungsten-halogen lamp	(33)

Table 14 Furnace temperature programs in pyrolytically-coated tubes.

Ref.	*Drying (°C)*	*Ramp (s)*	*Hold (s)*	*Ashing (°C)*	*Ramp (s)*	*Hold (s)*	*Atomizing (°C)*	*Ramp (s)*	*Hold (s)*
(32)	150	2	15	1100	10	10	2650	—	4
(21)	100	—	—	1000	—	25	2700	—	5
(20)*	120	10	10	1600	0–1	5–10	2500	1	3
(33)	140	10	20	1350	15	30	2700	0	4
(28)	140	10	10	1200	10	40	2400	0	3
(39)	120	5	10	600	10	10	2700	1	4
(24)	—	—	—	1200	—	—	2700	—	—
(41)	100	—	60	800	—	20	2700	—	3
(74)*	100	10	10	—	—	—	2400	10	2
(81)	160	5	20	1400	5	20	2300	0	5
(82)*	—	—	—	1250	—	—	2600	—	—
(34)*	200	30	10	1300	10	40	2700	0	10
(36)*	140	—	40	—	—	—	—	—	—
(71)	110	—	30	1100	—	5	2500	—	2

* Using L'vov platform.

In other samples such as blood, the background absorption during the determination of chromium was very small, so in this case the determinations may be carried out using a deuterium background correction system[28].

Another important parameter is the furnace program. The different furnace programs are shown in Table 14.

In general, the ranges of temperature used are: drying, 100–200°C; ashing, 600–1600°C; atomization, 2300–2700°C.

Hoening[71], proposed a quicker volatilisation of the analyte with a cooling procedure before the atomization step.

Study of interferences

Cationic and anionic interferences as well as the influence of organic solvents have been reported. Table 15 summarizes the most important interferences and their effects.

Table 15 Interferences in pyrolytically-coated tubes.

Interferent	*Observed effect*	*Matrix modifiers*
Na, Ca	Enhancing in HNO_3 (41) Depressing in HCl (41)	$Mg(NO_3)_2$ (33, 34) Standard addition method recommended (28)
K	Enhancing in HNO_3 (41)	Standard addition (28)
Fe	Enhancing in both HCl and HNO_3 (41)	$Mg(NO_3)_2$ (33, 34)
SO_4^{2-}	Enhancing effect (72)	$Mg(NO_3)_2$ (33, 34)
PO_4^{3-}	Depressing effect (72)	
With L'vov platform halides	Variable effects depending on experimental conditions	Not described

Cationic interferences. Brescianini[41] evaluated the interactions of elements such as Na, K, Ca and Fe in the analysis of welding fumes in both nitric and hydrochloric media. In nitric acid, an enhancement of the signal was observed, and in hydrochloric medium, Fe gave an enhancing effect and Ca and Na led to a depressing effect.

Anionic interferences. Anionic interferences were described by Castillo[72] who found that sulphates increase the absorption signal of chromium while phosphates reduce it, if compared with the absorption signals obtained by atomizing chromium in chloride and nitrate matrices and as dichromate.

Organic solvents. The effect of organic solvents has also been studied. Castillo[72] showed that different factors such as contact surface between sample and graphite, solvent ability to penetrate in the graphite and formation of compounds with the graphite and the analyte, influence the amplitude of the atomic absorption signal when Cr atomization is carried out with organic solvents.

Removal of the interferences. The interferences are in general overcame by the use of a matrix modifier or by the addition standard method. Veillon[33,34] used magnesium nitrate as matrix modifier/ashing aid in the analysis of human serum, and Dube[28] recommended the method of standard additions to minimize the matrix interferences and the effect of graphite tube aging in urine samples.

Some authors did not mention any kind of problems when using pyrolytically-coated tubes: Ramos[39], showed that these tubes are necessary for urban particulate matter determination in order to minimize memory effects.

Quality parameters

There are many data in the literature with reference to accuracy, precision and limits of detection for pyrolytically-coated tubes. The data are shown in Table 16.

With respect to recovery, Dube[28] found values ranging from 96 to 107.4% in urine and blood samples and Nakashima[13] gave results of 99.4% of recovery in acid solutions of sea water samples.

Table 16 Quality parameters in pyrolytically-coated tubes.

Ref.	*D. L. (Calcul)*	*D. L. (Value) (ng g^{-1})*	*RSD (%) day-to-day*	*RSD (%) long-time*
(32)	$2S_0$	0.2–0.4	—	4.2–6.7
(11)	$2S_0$	0.04	7	—
(28)	$3S_0$	0.09	10	7–12
(39)	—	20 pg	—	—
(24)	—	0.03	—	—

Pyrolytically-coated tubes and L'vov platform

The vaporization of the samples from a small graphite platform (L'vov platform) has been shown to significantly decrease matrix interferences in graphite furnace atomic absorption spectrometry[20].

In general, the use of magnesium nitrate as matrix modifier eliminates the interfering effect of cations, anions and acids. Lewis[34] determined different transition metals simultaneously, using $Mg(NO_3)_2$ as a matrix modifier/ashing aid/bulking agent, and ashing at high temperature. In a similar way, Fishman[73] and Betts[36] did not observe any interferences in the analysis of water of low ionic strength or in acidic tissue samples.

The only interference mentioned in the literature was the enhancement effect found by Matousek[74] in the presence of halides under certain experimental conditions. Thermal pretreatment of Cr_2O_3 to form Cr_2C_3, followed by subsequent atomization in the presence of $CuCl_2$ (on wall or platform), may significantly enhance the analyte absorbance. In contrast, without this thermal pretreatment, a $CuCl_2$ matrix would significantly supress chromium absorbance.

Studies of quality parameters in methods involving pyrolytically-coated tubes and L'vov platform are described in the literature. Bettinelli[20] described two approaches to evaluate the accuracy and precision in the determination of Cr in sediments, namely a standard addition method, and a direct comparison of the integrated signals from sediment solutions with those from a calibration graph. The authors concluded that, in disagreement with other reports, no background signals are encountered in chromium determinations and direct calibration can be used.

On the other hand, Lewis[34] gave a precision of 23% and a long term precision of 32% in blood serum samples.

Detection limits are listed in Table 17.

Uncoated vs. pyrolytically-coated tubes

Several studies have been undertaken to compare the results between uncoated and pyrolytically-coated tubes. In general, there are not many differences in the values with respect to instrumental conditions, except for atomizing temperatures (Table 18). The furnace programs used are shown in Table 19.

The effects of instrumental conditions on chromium absorbance in both tubes have been studied, ashing and atomizing temperatures being the main parameters mentioned. In fact, it has been shown that pyrolytically-coated tubes enhance the

Table 17 Detection limits for pyrolytic tubes and L'vov platform.

Kind of sample	*Reference*	*Replicates*	*D. L. Value*
Standard solutions	(82)	4	3.9 pg
Acidic tissues sol.	(36)	—	0.03 $\mu g\ g^{-1}$
Nitric sol. blood	(34)	12	0.37 $ng\ g^{-1}$

Table 18 Instrumental parameters in uncoated and pyrolytic tubes.

Parameter	*Values*	*References*
Sample volume (μl)	1	(66)
	20	(75)(77)
Sample introduction	Micropipettes	(75)
	Autosampler	(80)(76)(77)
Inert gas	Ar interrupted atom.	(80)(76)
	N_2	(66)
Background corrector	Deuterium	(80)
	Tungsten continuum source	(80)(77)

absorption signal by a factor of nearly two with respect to uncoated tubes, up to an ashing temperature of 1500 K[75].

The faster heating rate in the atomization step was shown to give higher sensitivity[76,77], and significantly reduce the optimum temperature according to Fernández[76].

With regard to chromium amounts retained in the graphite tubes, it seems that pyrolytically-coated tubes retained about 12% less chromium than uncoated ones, although the amount of chromium retained is variable depending on sample matrix. This illustrates the risk of inherent error in comparing samples and standards with different matrix composition and the necessity of using the standard addition method[27].

Study of the interferences

The interferences mentioned in the literature are mainly cationic, acidic as well as refractory chromium carbides. The most important are shown in Table 20.

Cationic interferences. Some authors found that transition and alkali metals cause variable effects on the chromium absorbance signal in the two tubes. According to Van Schoor[77], Ca, Cd, Fe, Ba, Ni, Hg(I) and Na are enhancing elements, and Pb, Sn, Hg(II), Mn, Cu, Co, K and Mg give depressing effects. However, Zn and Li do

Table 19 Furnace temperature programs in uncoated and pyrolytic tubes.

Ref.	*Drying (°C)*	*Ramp (s)*	*Hold (s)*	*Ashing (°C)*	*Ramp (s)*	*Hold (s)*	*Atomizing (°C)*	*Ramp (s)*	*Hold (s)*
(76)	—	—	—	—	—	—	2600–2900	—	—
(75)	147	—	60	727–2200	—	30–600	2827	—	5
(77)*	—	—	—	1300	—	30	2500	—	6
(67)	97	10	10	1800	3	2–3	2500	2	2
(80)	200	40	5	Variable	30	5	2450	0	5

* Using L'vov platform.

Table 20 Interferences in comparative studies of uncoated and pyrolytically-coated tubes.

Interferent	*Observed effect*	*Matrix modifier*
Ca, Cd, Fe, Ba, Ni, Hg(I), Na	Enhancing (77)	—
Pb, Sn, Hg(II), Mn, Cu, Co, K, Mg	Depressing (77)	
Zn, Li	Slight effect (77)	
$Cl^-(H^+, NH_4^+, Mg^{2+})$	Enhancing (77)	—
$Cl^-(Na^+, K^+, Ca^{2+})$	Negligible (77)	
Cl^- (Cu^{2+}, Fe^{3+})	Depressing (77)	
$HClO_4$, HNO_3	Depressing (77)	—
H_2SO_4, HCl, H_3PO_4	Negligible (77)	
Chromium carbides	Incomplete analyte release (73)	Cl_2/N_2 mixture (66)

not raise major interferences. In addition, NH_4^+ and Mg were shown to give an enhancing effect when added as chlorides, whereas Na, K and Ca gave negligible or weak effects and Cu and Fe(III) led to strong negative effects.

Wedl[75] found that carbide-forming elements of groups IVA to VIA did not interfere. The slight effect of sodium may be eliminated by working over 1000 K during the ashing step.

Some of the background signal caused by these metals can be eliminated by optimizing the ashing temperature.

Interferences of acids. Van Schoor[77] showed that $HClO_4$ and HNO_3 severely decrease the absorption signal whereas H_2SO_4, HCl and H_3PO_4 have negligible effects.

Refractory chromium carbides. Several researchers have studied the formation of carbide and mixed carbide oxide phases on the graphite furnace as a function of both heating time and temperature. Formation of refractory metallic carbide by chromium seems to be responsible for incomplete analyte release.

Matousek[66] used Cl_2/N_2 mixtures to remove refractory chromium carbide deposits from uncoated and pyrolytic graphite-coated tubes. The method consisted of a chlorine injection made through a drilled graphite electrode, and the removal of carbides was achieved by thermal chlorination between each analytical measure or during the later stage of the atomization process.

Conclusions

It is observed that the pyrolytic graphite tube does not always give higher sensitivity in comparison with the non-pyrolytic graphite tube. Brown[78] compared uncoated tubes, pyrolytically-coated and tubes made totally from pyrolytic graphite (TPCs). The last ones increased the heating rate and improved sensitivity. On the other hand, pyrocoated tubes lasted significantly longer than the uncoated tube, 200 against 50 firings[77].

Table 21 Instrumental parameters in comparative studies of the different kinds of tubes.

Parameter	*Value*	*References*
Slit-width (nm)	0.2	(79)
	0.7	(30)
Sample volume (μl)	10	(78)(30)
	20	(8)(79)
Sample introduction	Micropipettes	(79)
	Autosampler	(30)
Inert gas	Ar	(80)(79)(30)(8)
Background corrector	Deuterium arc	(8)

Uncoated tubes vs. pyrolytically-coated vs. metal-coated

Different comparative studies about chromium behaviour in different tubes have been described in the literature: uncoated, pyrolytically-coated and W or Zr-coated tubes.

The instrumental parameters are the same for all kinds of tubes. They are shown in Table 21 and the furnace programs used are presented in Table 22.

Depending on furnace types, the optimum temperatures for each step may change. Arpadjan[67], found that with tungsten-impregnated tubes, temperatures up to 1500°C may be applied during the pretreatment step, whereas Pyrzynska[79] showed that no losses of analyte occurred when ashing temperatures of 1200°C or 900°C were used.

Study of the interferences

The most important interferences are shown in Table 23.

Cationic interferences. Metals such as iron, cobalt and copper, which have a volatility similar to that of chromium show large interferences in all kinds of tubes with different effects, and lead, aluminium and calcium, display also variable influences[79]. On the other hand, Arpadjan[67] demonstrated that the use of Na_2WO_4 and Na_2MoO_4 as matrix modifiers eliminate interferences.

Interferences of acids. Hydrochloric acid slightly influences the chromium signal and perchloric and nitric acids cause depressing effects, especially when uncoated tubes are used.

Table 22 Furnace temperature programs in different kinds of tubes.

Ref.	*Drying (°C)*	*Ramp (s)*	*Hold (s)*	*Ashing (°C)*	*Ramp (s)*	*Hold (s)*	*Atomizing (°C)*	*Ramp (s)*	*Hold (s)*
(8)	130	20	40	1200	10	40	2700	1	10
(67)	120	20	40	1000–1700	20	40	2500–2700	1-4	5
(30	—	—	—	900	—	—	2600–2700	—	—

Table 23 Interferences in comparative studies of uncoated, pyrolytically-coated and metal-coated tubes.

Interferent	*Observed effect*	*Matrix modifiers*
Fe, Co, Cu	Large interferences (79)	Na_2WO_4 (67)
Pb, Al, Ca	Interferences (79)	Na_2MoO_4 (67)
HCl	Slight interference (79)	—
H_2SO_4	Enhancing (79)	

Sulphuric acid above 1 mol l^{-1} concentration, was shown to produce an enhancing effect[79].

Quality parameters

Pyrzynska[79] found the best analytical parameters (sensitivity, detection limits and RSD), when using pyrolytically-coated tubes. When metal-coated tubes are used, some improvements can be achieved in comparison with uncoated tubes, which rise to poorest sensitivity and detection limit. However, the lifetime of metal carbide coated tubes is about twice as long as that of pyrolytically-coated.

SOLID SAMPLING GFAAS

Schlemmer[38] studied the introduction of solid samples into an electrothermal atomizer. The interferences observed in the analysis of solid samples seemed to be more difficult to remove than in the analysis of solutions, due to the dependence of the atomization rate on the construction of the atomizer and on the volatility of the matrix. This author showed that, if the matrix is refractory and cannot be separated from the analyte it influences the atomization rate. In addition, if the matrix is volatilized together with the analyte, the residence time in the tube is reduced and the peak height is also affected.

The author determined chromium as well as other heavy metals in urban particulate matter reference materials. These measurements were made by introducing approximately 0.7 to 1.0 mg of the solid sample into the furnace. Atomization from the L'vov platform was recommended for chromium. The signal obtained was symmetric without pronounced tailing when measured at 425.4 nm. This author is the only one who uses this wavelength to study the chromium behaviour in AAS.

CERTIFIED REFERENCE MATERIALS FOR THE QUALITY CONTROL OF Cr DETERMINATION IN THE ENVIRONMENT

The growing international concern about the environmental risk caused by toxic heavy metals has led to the implementation of EC Directives or international conventions (e.g. Paris and Oslo convention for the North Sea and Barcelona convention for the Mediterranean Sea) for the monitoring of these elements in the terrestrial and aquatic environments. The effect of these actions are evaluated on the basis of analyses of different environmental matrices conducted over long periods of time. Long term trends and in some cases kinetics of decontamination processes may therefore be assessed. Decisions are taken as a result of these monitoring surveys and may have a strong economic impact (e.g. closing of factories, waste management, etc). Consequently, the results of analysis on which the decisions rely have to be the most accurate.

In view of the strong need for the control of the quality of analysis in the environment, the Commission of the European Communities has undertaken, through the Community Bureau of Reference (BCR), the organization of intercomparisons involving 20 to 30 well trained and selected European laboratories using a wide variety of analytical techniques. The achievement of these exercises is the production of a wide range of certified reference materials (CRMs) for the improvement of accuracy and measurement harmony in various areas of concern at European Community level[83]. The BCR has already completed a series of projects and CRMs for trace metals analysis in different environmental systems have been produced. However, in most cases the results of Cr determinations could not be accepted because the spread of results between the different laboratories and/or analytical techniques was too large or a methodological bias could not be excluded. The list of CRMs in which Cr could be certified is given in Table 24 along with reference materials produced by the National Institute for Environmental Studies (NIES, Japan), the National Institute of Standards and Technology (NIST, USA) and the

Table 24 Certified reference materials for Cr determination.

RM	*Matrix*	*Conc. ($\mu g\ g^{-1}$)*	*Origin*
CRM 032	Phosphate rock	257 ± 16	BCR
CRM 040	Blend coal	31.3 ± 2.0	BCR
CRM 176	City waste incin. ash	863 ± 30	BCR
CRM 277	Estuarine sediment	192 ± 7	BCR
CRM 278	Mussel tissue	0.80 ± 0.08	BCR
CRM 280	Lake sediment	114 ± 4	BCR
CRM 320	River sediment	138 ± 7	BCR
No. 2	Pond sediment	75 ± 5	NIES
No. 6	Mussel tissue	0.63 ± 0.07	NIES
No. 8	Vehicle exhaust part.	25.5 ± 1.5	NIES
1566a	Oyster tissue	0.69 ± 0.27	NIST
1572	Citrus leaves	0.8 ± 0.2	NIST
1633a	Coal fly ash	196 ± 6	NIST
1646	Estuarine sediment	76 ± 3	NIST
1648	Urban partic. matter	403 ± 12	NIST
CASS-2	Nearshore water	0.121 ± 0.016	NRCC
NASS-2	Open ocean sea water	0.175 ± 0.010	NRCC
SLEW-1	Estuarine sediment	0.139 ± 0.016	NRCC
SLRS-1	River water	0.36 ± 0.04	NRCC
BCSS-1	Marine sediment	123 ± 14	NRCC
MESS-1	Marine sediment	71 ± 11	NRCC
PACS-1	Marine sediment	113 ± 8	NRCC
DOLT-1	Dogfish liver	0.40 ± 0.07	NRCC
DORM-1	Dogfish muscle	3.60 ± 0.40	NRCC

National Research Council of Canada (NRCC). A project is currently conducted by the BCR for the identification of its reference materials for which an additional certification of Cr would be useful; the techniques of final determinations used for the previous BCR-certifications were electrothermal atomic absorption spectrometry (ETAAS), ETAAS with Zeeman background correction (ZETAAS), inductively coupled plasma atomic emission spectrometry (ICPAES), instrumental neutron activation analysis (INAA) and isotope dilution mass spectrometry (IDMS).

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