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REVIEW

Analysis and Speciation of Chromium in Environmental Matrices by Various Analytical Techniques

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Chromium is a very important metal due to its use in various industries, such as dye, pigments and stainless steel. Hexavalent chromium is a carcinogen. Its determination in various environmental segments is always a challenging issue for environmental researchers. In this concern first section of this review article gives a brief history of chromium, such as its oxidation states, production information, uses, biological importance, exposure pathways and regulatory concentration levels. The second section explains about the sources of chromium and the next section gives the details of health effects and toxicity caused due to the presence of chromium in various environmental segments. Finally, this paper discusses the determination of chromium in different biological and environmental samples by various analytical techniques, such as atomic absorption spectrometer, Spectrophotometer, Voltammeter, Inductively coupled plasma techniques (ICP-AES, OES), potentiometer, spectrofluorometer, HPLC/GC-MS and chemiluminescence reported by the researchers worldwide since 2006. All the data collected during the literature survey is tabulated, which gives important information about the analytical methods and techniques used for the chromium determination.

Key Words: Chromium, Hexavalent chromium, Analytical techniques, Biological and Environmental samples.

INTRODUCTION

Chromium is a very important trace element in regarding both environmental and biological point of view. Most of the research about chromium focused on the biological activity of trivalent chromium and carcinogenicity of hexavalent chromium. It is a lustrous and hard metal that takes high polish and have high melting point[1]. In 1798, a French chemist Nicholas-Louis Vauquelin successfully isolated metallic chromium by heating chromic oxide with charcoal by means of chemical reduction[2].

Chromium oxidation states are ranging from -2 to +6. But in nature it exists in only three oxidation states. Those three oxidation states of Cr are 0, +3 and +6. It exists in 0 oxidation state in metallic Cr, in chromic compounds it is in +3 states and in CrO_4^{2-}, $Cr_2O_7^{2-}$ compounds it exists in +6 oxidation state. Among all oxidation states, +3 and +6 states are more commonly observed in chromium compounds but the remaining oxidation states are rare[3].

According to the International Minerals Association, 82 minerals were recognized for chromium. Among these, the important chromium mineral is chromite. The concentration of chromium in chromite mineral is 46.46 % on average[2]. Most of the chromium ore in the world are producing from South Africa, India and Kazakhstan. The overall production of chromium ore in all over the world in 2008 was 6,950 thousand metric tons, but over 74 % was produced in the above mentioned countries[4]. Chromium, over 90 % in its production is using in metallurgical industries particularly in stainless steel and nonferrous alloys. Only 5 % of chromium is using in chemical industries and the remaining is using in refractories and foundries[5]. In addition to the above, chromium is also useful in dye and pigment as in the form of lead chromate. chromium(VI) salts are used for the preservation of wood[6]. Potassium dichromate is also useful in photography[2].

Among all chromium compounds, there is a sufficient evidence for the carcinogenicity of chromium(VI) compounds. It may mostly encounter to the workers at chromate production and chromium plating industries. Based on the research evidences on animals the International Agency for research on cancer[7] has included hexavalent chromium as group I carcinogen (carcinogenic to human) and the U.S. EPA included it as group A carcinogen through inhalation route[8,9]. Chromium(III) is an important component in balanced human and animal diet. The deficiency of chromium(III) can cause

the disturbances in glucose and lipid metabolism in humans as well as in animals[10]. There is some experimental evidence about the chromium role in thyroid metabolism in humans and animals. Trivalent chromium has also interaction with the insulin and its receptors, but not much more evidence is available about the above mentioned interactions[11]. Haylock *et al.*[12] reported about the biological activity of some trivalent chromium complexes, such as the relationship of chromium to the glucose tolerance factor II. Hwang *et al.*[13] reported the insulin-like activity of trivalent chromium binding fractions from brewer's yeast. The minimum levels of trivalent chromium for human health is unknown but the requirement for the safe and adequate human life, the daily ingestion of 50 μg L^{-1} to 200 μg L^{-1} is required[2]. Chromium mainly enters into the human bodies in so many ways, such as through drinking water, surface water and dermal contact and inhalation routes. The inhalation route exposure more likely happens to the workers in industries such as welding, cutting and heating of chromium alloys. Dermal absorption of chromium to the workers in the previously mentioned industries was reported by many researchers[14-16]. Chromate ion can enters into the human bloodstream through breaks in the skin and causes blood poisoning when it destroys red blood corpuscles[2]. The population residing at near the anthropogenic sources of chromium(VI) may be exposed through inhalation of ambient air or ingestion of contaminated drinking water[17].

According to the USEPA, the maximum contaminant level for total chromium in drinking water is 100 μg mL^{-1}. In soil, the limits are 390 mg kg^{-1} for ingestion, 270 mg kg^{-1} for inhalation and 2.0 mg kg^{-1} for migration to the ground water[18]. According to the California EPA[2], the maximum contaminant for total chromium in drinking water is 50 μg mL^{-1}. But the chronic reference exposure level of hexavalent chromium in ambient air is 200 ng m^{-3}. The chronic reference exposure level is a concentration in air at which no adverse non-cancer health effects are expected[19]. The California EPA introduces the public health goal (level of contaminant in drinking water that does not cause a significant health risk) for hexavalent chromium as 0.06 ppb[20].

Few researchers reviewed the determination of chromium in various samples by various analytical techniques. Rubio *et al.*[21] reviewed the determination of chromium in environmental and biological samples by atomic absorption spectroscopy. But the Gomez and Callao[22] reviewed the chromium determination in various samples by different analytical techniques. They considered around five year's research regarding chromium. Saha and Orvig[23] reviewed the application of biosorbents for the elimination of hexavalent chromium from industrial and municipal effluents. Bobrowske *et al.*[24] reviewed the determination and speciation of chromium by voltammetry. Pyrzynska[25] reviewed the sorption principles for use in chromium speciation analysis. Camel[26] reviewed the solid phase extraction of trace elements, which was inclusive of chromium.

A review about the determination of chromium by various analytical techniques was published in 2006[22], due to this we focused to present the data produced after the year 2006. This review paper summarizes the analytical techniques and their progress in recent years about the recovery and determination of chromium in various environmental and biological samples.

Source of chromium: Industrial and mining activities are main source of chromium contamination in the worldwide. The widely use of chromium for making of alloys which were used for dental casting such as Ni-Cr, Co-Cr Ti-Cr and stainless steel[27], leather tanning, electroplating and electroplating baths (operates at elevated temperatures causes for the productions of moist chromic acid into the environment, which is familiar sources of it in the U.S.[28,29]), chrome plating, wood processing such as the construction of buildings, play ground equipment, furniture,flower beds, control agent for corrosion and in many drug preparations, are the main sources for the release of Cr into the environment[30]. The improper industrial waste disposal practices caused for accumulating of chromium in soil and increase the instant contaminations in both surface and ground water resources around the world. However, high range of utilization and inappropriate disposal of chromium waste products, especially animal waste deposition and its alloy's along with essential and non essential elements[31,32] have created the abundant sources of chromium pollution. Another main source is water, where the chromium exists as oxyanions, such as chromate ($HCrO_4^-$) dichromate ($Cr_2O_7^{2-}$) and chromic acid (H_2CrO_4) depends on pH of the system[33,34]. It was released into the environment from plants due to daily intake of some trace amount of metal ions to maintain their regular functions. Some food products also released chromium into the environment. Medicated and non medicated soaps and creams which are used in our daily lives also one of chromium sources which causes skin allergy and pollute the environment[35,36]. The micronutrients and dietary supplements industries have widely used hexavalent chromium compounds, such as chromium chloride, niacin-bound chromium or chromium polynicotinate and chromium picolynate and were being toxic and carcinogenic to animals and humans[37].

Health effects and toxicity: Chromium was listed as 8th metal in accordance with its toxicity in top 50 toxic substances by the agency for toxic substances and disease registry[38-42]. Among all other oxidation states of chromium, hexavalent of chromium is more toxic by its high level of oxidation property and was involved in many metabolic redox and hydrolysis reactions in the biological systems and was cause for human mutagenic and carcinogenicity[43,44]. Irritation or damage to the eyes and skin may happen due to contact of hexavalent chromium with these organs[45]. It can cause the lung cancer to the workers who breathe airborne hexavalent chromium. The effect of hexavalent chromium on bronchial epithelial cells may be the reason for lung cancer[46,47]. For example lead chromate and sodium chromate, have been associated with lung cancer and respiratory tract toxicity by genomic interactions in cells to release extracellular Cr and Pb ions[48-51]. It damages the proteins, precipitates the nucleic acids and interfere with normal enzymatic activity through reduction to trivalent form which form complexes with intracellular macromolecules including genetic material and responsible for its toxic and mutagenic properties[52-55]. For example, cytogenetic damage by micronuclei induction in erythrocyte cells,

depletion of liver and muscle glycogen along with decreased leukocyte counts in crabs[56-58], respiratory inhibition in trout liver of mitochondria by reduction of Cr^{6+} to Cr^{3+}. Chromium exposure to cell cultured system causes chromosomal damage which affected the biological systems functions by involving with gene induction instead of affecting constitutive gene expression. The epigenetic changes in mechanism may cause the changes in phosphorylation, altered DNA methylation status, histone acetylation and signaling path ways have been observed[59-61]. It may also affect the kidney, histology of tissues and made pathological changes in spleen and blood. For example, kidney and liver of teleost fish, Channa puncatata were damaged due to exposure to hexavalent chromium[31]. Hexavalent chromium, a pulmonary irritant, which may probably mediated by the reactive oxygen species (ROSs) generated during its reduction and cause fibro proliferative diseases and air way hypersensitivity[62-64]. It also reacts with biological reductants, such as ascorbate and thiols, often generate free radicals, which in turn activate O_2 and produce reactive oxygen species, including hydroxyl radicals, singlet oxygen, superoxide and hydrogen peroxide[65-68]. This may lead to oxidative stress, damaging DNA and proteins by the formation of chromium-DNA adduct and DNA-protein cross-links with the help of excessive reactive oxygen species[69-74].

The exposure of Cr compounds in rats causes DNA damage, apoptosis and inflammation to lungs[75-78]. The exposure of human bronchial BEAS-2B cells with Cr(VI) followed by As(III) increases apoptosis and disrupts membrane integrity[30]. It may also damages the DNA which is association with erythrocytes, urinary 8-OHdG levels, olive tail moment, tail length and tail DNA %. It also affects the lymphocyte in peripheral blood of neonates may caused for cancer-causing gene mutations. Especially it has been seen in the workers who are working in electroplating industries[54]. The chromium exposure also decreases the concentration of essential metal ions in blood results an adverse health impacts in humans. In aqueous solution Cr(VI) predominately exists as chromate ion[33] and easily penetrates into biological membranes and cause cellular damage by inducing oxidative stress[79,80]. If Cr(VI) is more than its permeable level (0.05 mg/L) in the domestic water supplies which was set by the US EPA and the European Union[81], was causes severe diarrhea, ulcers, eye and skin irritation, kidney dysfunction and probably lung carcinoma by accumulating in living tissues throughout the food chain due to its non-biodegradable metallic nature[82,83]. It may also cause renal tubular necrosis, chronic ulceration and perforation of the nasal septum[84]. The National Toxicological Program of the United States of America reported the cancer or significant tumors in rats by oral ingestion of hexavalent chromium[85]. In ambient air, the level of 1 ng m^{-3} of hexavalent chromium causes 150 additional cancer cases when they exposed over a 70-year-lifetime[86]. Many authors and environmental agencies such as NIOSH (National Institute for occupational safety and health) reviewed about the toxicity and carcinogenicity of chromium and chromium compounds[87-89].

Various analytical techniques have been using in worldwide for the determination of hexavalent, trivalent and total chromium. Total chromium can be determined by using atomic absorption spectroscopy (AAS). Cr(III) and Cr(VI) can be detected by using ion chromatography (IC). EPA 218.6 analytical method can be used for the determination of chromium in drinking water. SW 7196A or SW 7199 methods can be applied for the determination of chromium in wastewater. Hexavalent chromium can also be determined by UV visible spectrophotometer[2].

The literature survey collected about the determination of chromium including hexavalent chromium with various analytical techniques is presented in Table-1[90-221]. This literature survey revealed that most of the researchers were interested in atomic absorption spectroscopy techniques, such as flame atomic absorption spectrometer, graphite furnace atomic absorption spectrometer and electrothermal atomic absorption spectrometer. We made a pie chart about the percentage of papers described about the various analytical techniques to determine the chromium in different samples. From the Fig. 1, it is clear that the researchers used atomic absorption spectroscopy techniques over 50 %. After that the atomic absorption spectroscopy techniques, the priority of the researchers for analytical techniques is as follows: spectrophotometer, volvammeter, inductively coupled plasma techniques such as, ICP-OES, AES and MS, potentiometer, spectrofluorometer, HPLC/GC and Chemiluminescence. Regarding the analytical methods mostly the researchers used adsorption and liquid-liquid extraction. Few of them were concentrated on some electrochemical principles. Nitrogen compounds, such as amine derivatives, azo compounds, isoxazolones, pyrazolones phenyl amines and carbazides are widely used for the recovery/separation of chromium from various samples, due to the strong complex ability of nitrogen. A few researchers reported various groups functionalized resin, xanthates, amberlite derivates and activated carbons for the pre-concentration of it. A few were used thionyl compounds, phosphorus compounds, crown ethers, carbonyl derivates such as trifluroacetyl acetone, thio-ethers, quinolines and other reagents. Mostly, these were applied for the recovery of chromium from aqueous samples, agricultural and biological samples.

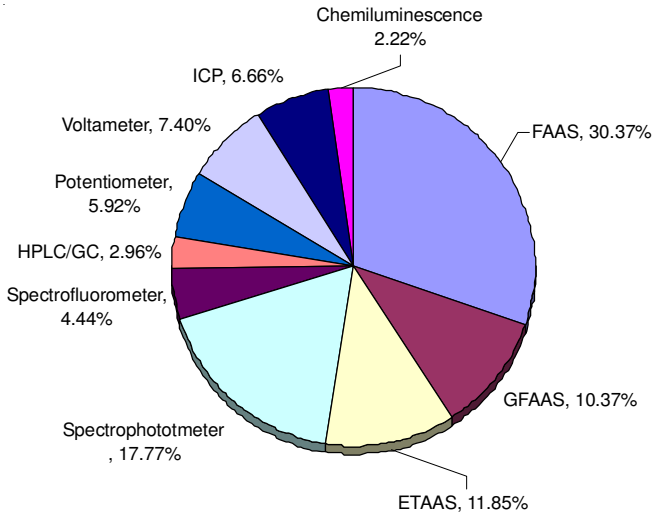

Fig. 1. Utilization of various analytical techniques for the determination of chromium since 2006

TABLE-1
DETERMINATION OF CHROMIUM BY USING VARIOUS ANALYTICAL TECHNIQUES

S. No	Analyte	Analytical Instrument used for the detection	Method	Limit of Detection (LOD)	Matrix	Supporting media	Ref
1	Cr total Cr(VI) Cr(III)	AAS	Adsorption	-	Waste water	Aniline formaldehyde condesate	90
2	Cr(III), Cr(VI)	AAS	Co -precipitation	1.0 μg L^{-1} for Cr(III)	Spiked Natural water samples	3-Ethyl-4-(*p*-chloroben-zylidenamino-4,5-dihydro-1H-1,2,4-triazol-5-one	91
3	Cr(III)	FAAS	Pre concentration	-	Water samples	5-chloro-2-hydroxy aniline	92
4	Cr(III), Cr(VI)	FAAS	Solid-phase extraction	0.51 ng mL^{-1} for Cr(VI)	Drinking water, surface water and industrial waste water effluents	Nickel-aluminum layered double hydroxide	93
5	Cr(III), Cr(VI)	AAS	Solid-phase extraction	0.6 μg L^{-1} for Cr(III), 0.9 μg L^{-1} for Cr(VI)	Waste water	Azophenol carboxylate	94
6	Cr(III), Cr(VI)	FAAS	Preconcentration	0.01 μg L^{-1} for Cr(III)	Water and food samples	Poly-2-(5-methyl - isoxazole)	95
7	Cr(III), Cr(VI)	FAAS	Preconcentration	0.3 μg L^{-1} for Cr(III), Cr(VI)	Drinking water samples	Llama (lama glama) fibres	96
8	Cr(III), Cr(VI)	FAAS	Solid-phase extraction	7.7 μg L^{-1} for Cr(VI), 8.6 μg L^{-1} for Cr total	Food, water and pharmaceutical samples	Amberlite XAD-1180 resin	97
9	Cr(III)	FAAS	Electrochemical oxidation	-	Waste water tanning baths	Doehlert matrix	98
10	Cr(III), Cr(VI)	ET AAS	Mixed micelle cloud point extraction	1 ng L^{-1} for Cr(VI)	Tap water and River water samples	Sodium dodecyl sulphate and triton X-114	99
11	Cr(III), Cr(VI)	FAAS	Bio separation	1.58 μg L^{-1} for Cr(III)	Natural and Industrial waters and tobacco leaves	Olive pomace (pyrolyzed)	100
12	Cr(III), Cr(VI)	FAAS	Carrier element-free coprecipitation	0.7 μg L^{-1} for Cr(III)	Drinking water and soil samples	5-Chloro-3-[4-(trifluoro methoxy) phenylimino] indolin-2-one	101
13	Cr(III)	FAAS	Solid phase extraction	4.08 μg L^{-1}	Food and herbal plant samples	Single-walled carbon nanotubes	102
14	Cr total	ET AAS	In vitro	4.0 pg	Food samples (convenience and fast foods)	-	103
15	Cr total	GF AAS	Microwave digestion	-	Food samples (convenience and fast foods)	-	104
16	Cr total	GF AAS	Slurry sampling	86.6 ng g^{-1} of the slurry	Plant samples and Certified reference materials	Ir/Nb modifier	105
17	Cr total	ET AAS	Solid sampling	-	Pharmaceutical grade barium sulphate	-	106
18	Cr(III), Cr(VI)	FAAS	Solid phase extraction	1.94 μg L^{-1} for Cr(VI)	Tap water, river water and electroplating water samples	Dowex M 4195	107
19	Cr(III), Cr(VI)	AAS	Solid phase extraction	0.75 μg L^{-1} for Cr(III)	Natural waters, Turkish tobacco, coffee and soil samples	Chromosorb 108	108
20	Cr(III)	GF AAS	Cloud point extraction	0.02 μg L^{-1}	Human serum	1-(2-Pyridylazo)-2-naphthol	109
21	Cr total	ET AAS	Thermal stabilization	0.45 μg L^{-1}	Waters from petroleum exploration	Pd and HF as chemical modifiers	110
22	Cr total	ET AAS	EPA method 1669 and APDC-MIBK extraction method	-	Ground water samples containing iron	-	111
23	Cr(VI)	AAS	Biosorption	-	Aqueous solution	Bacterial biofilm supported on granular activated carbon	112
24	Cr total	ET AAS	Pyrolysis and atomization	3.4 μg L^{-1}	Marine sediment slurry samples	Zirconium as permanent modifier	113
25	Cr(III)	ET AAS	Capillary micro extraction	0.02 ng mL^{-1}	Natural water samples	Nanometer zirconium phosphate	114

S. No	Analyte	Analytical Instrument used for the detection	Method	Limit of Detection (LOD)	Matrix	Supporting media	Ref
26	Cr(III)	GF AAS	Continuous- flow micro extraction	45 ng L^{-1}	Water samples	8-Hydroxyquinoline	115
27	Cr(III)	GF AAS	-	0.81 μg L^{-1}	Slurries of fish feces	Triton X-100	116
28	Cr total	GF AAS	Sequential extraction and microwave- acid digestion	-	*Mentha piperita* L. and soil samples	-	117
29	Cr(VI)	FAAS	On-line sorption preconcentration	0.4 μg L^{-1}	Water samples	Poly-chlorotrifluoro ethylene beads	118
30	Cr(VI)	GF AAS	Acid digestion	0.02 μg L^{-1}	Black, green and herbal tea samples	Sodium carbonate	119
31	Cr(III)	FAAS	Preconcentration	2.0 ng mL^{-1}	Water and fish samples	*Penicillium digitatum*	120
32	Cr total	ET AAS	-	0.13 μg L^{-1}	*Orujo* spirit samples	Chemical modifiers	121
33	Cr(III) and total Cr	FAAS	Cloud point extraction	0.32 ng mL^{-1} for Cr(III)	Water samples	Triton X-100	122
34	Cr(VI)	Colourimeter	Liquid –liquid extraction	1.5-0.5 μg L^{-1}	Environmental air	Diphenylcarbazide	123
	Cr(VI)	ET AAS	Solvent extraction	0.2 μg L^{-1}	Exhaled breath condensate	Tetra butyl ammonium ion	123
35	Cr(III), Cr(VI)	AAS	Co precipitation	0.65 μg L^{-1} for Cr(III) and 0.78 μg L^{-1} for Cr(VI)	Tap waters	Dysprosium hydroxide	124
36	Cr(VI) and total Cr	ET AAS	Leaching with sodium carbonate for Cr(VI) and acid digestion for total Cr	0.2 ng m^{-3} for Cr(VI)	Atmospheric aerosols	-	125
37	Cr(VI)	AAS	Liquid-liquid extraction	-	Industrial waste solution	Cyanex 923 with kerosene	126
38	Cr(III)	FAAS	Magnetic solid phase extraction	0.69 ng mL^{-1}	Environmental and biological samples	Fe_3O_4@ZrO_2 nanoparticles	127
39	Cr(VI)	FAAS	Anionic liquid ion exchange	-	Electroplating effluent	Alamine 336 and refined palm oil	128
40	Cr(VI) and total Cr	Spectrophotometer for Cr(VI) and AAS for total Cr	Adsorption	-	Aqueous environment	Polyaniline synthesized on jute fiber	129
41	Cr total	GF AAS	Microwave digestion	-	Food stuffs, spices, beverages and nutrition supplements	-	130
42	Cr(VI)	FAAS	On-line separation and preconcentration	0.2 μg L^{-1}	Wastewater samples	Modified mesoporous silica materials	131
43	Cr(V) and total Cr	AAS	Solid phase extraction	0.90 μg L^{-1} for Cr(VI)	Natural water samples	Multiwalled carbon nanotubes	132
44	Cr(VI)	ET AAS	On-line dynamic extraction	-	Agriculture soil materials	Micro-sequential injection bead-injection lab-on-valve	133
45	Cr(III) Cr total	FAAS	On-line preconcentration	-	Synthetic mixtures and wastewater	8-Hydroxyquinoline micro column immobilized on surfactant coated alumina	134
46	Cr(III) Cr(VI)	FAAS	Preconcentration	49 ng L^{-1} for Cr(III) and 43 ng L^{-1} for Cr(VI)	Water samples	Octadecyl silica membrane disks	135
47	Cr(III) Cr(VI)	ET AAS	Preconcentration	0.02 μg L^{-1} for Cr(III) and 0.03 μg L^{-1} for Cr(VI)	River and tap water samples	Dual mini columns (*Chlorella vulgaris* and anion exchange resin)	136
48	Cr(III) Cr(VI)	ET AAS	Preconcentration	3.0 ng L^{-1}	Drinking water samples	Activated carbon	137
49	Cr(III)	FAAS	Solid phase extraction	0.02 ng mL^{-1}	Electroplating waste water samples	ENVI-18 DSK disks	138
50	Cr(VI)	ET AAS	Leaching	0.07 μg g^{-1}	Soil samples	Sodium phosphate	139
51	Cr(VI)	Spectrophotometer	Adsorption	-	Wastewater samples	Polyaniline synthesized on jute fiber	140
52	Cr(III) Cr(VI)	Spectrophotometer for Cr(VI) and FAAS for total Cr	Adsorption	-	Aqueous solutions	Activated carbon and char	141

S. No.	Analyte	Analytical Instrument used for the detection	Method	Limit of Detection (LOD)	Matrix	Supporting media	Ref
53	Cr(VI)	Spectrophotometer	Adsorption	-	Industrial wastewater effluents	Xanthated chitosan	142
54	Cr(III) Cr(VI)	AAS	Adsorption	1.2 μg L^{-1} for Cr(VI)	Industrial wastewater samples	Polyurethane foams	143
55	Cr(VI)	GF AAS	Leaching	0.93 μg L^{-1}	Plant leaves, soil and sediment samples	Sodium carbonate	144
56	Cr(VI)	ET AAS	Liquid-liquid micro extraction	0.07 ng mL^{-1}	Lake and tap water samples	Ammonium pyrrolidinedithio carbamate (APDC)	145
57	Cr(VI)	GF AAS	Liquid-liquid extraction	0.15 μg L^{-1}	Drinking water samples	2-[2-(4-Methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H-indolium chloride	146
58	Cr total	ET AAS	Preconcentration/separation	0.34 μg L^{-1}	Sea water and drinking waters	Gold coated TiO_2 nanoparticles	147
59	Cr(III)	AAS	Solid phase extraction	0.81 μg L^{-1}	Hot spring water and drinking waters	Amberlite XAD - 200	148
60	Cr(III)	GF AAS	Solid phase extraction	0.024 μg L^{-1}	Natural waters	*N,N-bis*-(-methyl salicylidene)-2,2-dimethyl-1,3-propane diimine	149
61	Cr(III) Cr(VI)	GF AAS	Solidified floating organic drop micro extraction	0.006 μg L^{-1} for Cr(III)	Tap water, well water, mineral water and urine samples	1-Undecanol containing 2-thenoyltrifluoro -acetone	150
62	Cr(III) Cr(VI)	FAAS	Co precipitation	1.33 μg L^{-1} for Cr(III)	natural water and food samples (fish, white cheese, cow's meat)	Ni2+/2-nitroso-1-naphthol-4-sulfonic acid	151
63	Cr(III) Cr(VI)	FAAS	Cloud point extraction	0.7 μg L^{-1} for Cr(III)	River water samples	1-(2-Pyridilazo)-2-naphtol	152
64	Cr(III) Cr(VI)	FAAS	Dispersive liquid-liquid micro extraction	0.08 μg L^{-1} for Cr(III) and 0.07 μg L^{-1} for total Cr	Tap water, river water and sea waters	-	153
65	Cr(III) Cr(VI)	GF AAS	Cloud point extraction	21 ng L^{-1} for Cr(III)	Natural water samples	1-Phenyl -3- methyl-4-benzoylpyrazol-5-one	154
66	Cr(III) Cr(VI)	FAAS	Solid phase extraction	52.4 ng L^{-1} for Cr(III)	Lake water and tap water samples	Chitosan-bound FeC nanoparticles	155
67	Cr(III) Cr(VI)	AAS	Co precipitation	1.1 μg L^{-1} for Cr(III)	Montana soil and water samples	Ytterbium(III) hydroxide	156
68	Cr(VI)	GF AAS	Liquid-liquid extraction	50 ng L^{-1}	Soil and water samples	Hydrogen peroxide/ ethyl acetate	157
69	Cr(III) Cr(VI)	FAAS	Selective solid phase extraction and pre concentration	-	Real water samples	Alumina phases-physically adsorbed-isatin-thiosemicarbazone	158
70	Cr(III)	AAS	Solvent extraction	-	-	Tri-*n*-butyl phosphate in kerosene diluent	159
71	Cr(III) Cr(VI)	FAAS	Co precipitation	0.87 μg L^{-1} for Cr(III) and 1.18 μg L^{-1} for Cr(VI)	Natural water samples and Sewage sludge (BCR-144R) sample	Thulium hydroxide	160
72	Cr(III)	AAS	Adsorption	-	-	Activated carbon from agriculture waste and activated carbon fabric cloth	161
73	Cr total	ET AAS	Precipitation	1.5 μg L^{-1}	Gasoline samples	cetyltrimethylammonium bromide	162
74	Cr(III) Cr(VI)	AAS	Solid phase extraction	0.02 μg L^{-1} for Cr(III) and 0.014 μg L^{-1} for Cr(VI)	Industrial water samples	Acetyl acetone modified XAD -16	163
75	Cr(VI)	Spectrophotometer	Solid phase extraction	5 μg L^{-1}	Electroplating wastewater and natural water	Cetyltrimethylammoniumbromide/ Diphenylcarbazide	164
76	Cr(VI)	Spectrophotometer	Solid phase extraction	6 μg L^{-1}	Electroplating wastewater and natural water	XAD-4/Diphenylcarbazide	165
77	Cr(III) Cr(VI)	HPLC	Cloud point extraction	7.5 μg L^{-1} for Cr(III), 3.5 μg L^{-1} for Cr(VI)	Sediment samples	1-(2-Thiazolylazo)-2-naphthol/Triton X-114	166

S. No.	Analyte	Analytical Instrument used for the detection	Method	Limit of Detection (LOD)	Matrix	Supporting media	Ref
78	Cr(III) Cr(VI)	HPLC	Complexation with ionic liquid and extraction	1.9 μg L^{-1} for Cr(III) 1.0 μg L^{-1} for Cr(VI)	Wastewater samples	1-Butyl-3-methy imida zolium hexafluoro phosphate/ ammonium pyrrolidinedithiocarbamate	167
79	Cr(III)	GC	Microwave-assisted derivatization and single-drop micro extraction	0.5 ng mL^{-1}	Natural water and industrial effluents	1,1,1-trifluoroacety-lacetone	168
80	Cr(III) Cr(VI)	HPTLC/LA-ICPMS	Volatilization with laser ablation	0.4 ng Cr(III), 6 ng for Cr(VI)	-	-	169
81	Cr(III)	Potentiometer	Coated wire electrode	6.8×10^{-8} M	Multivitamins, mineral water	1-(2-(1*H*-Imidazole-1-yl)-1-(4-Methoxy phenyl) ethylidene)-2-phenyl hydrazine	170
82	Cr(III)	Potentiometer	Ion selective electrode	5.6×10^{-8} M	Water and food samples	*N*-(Acetoacetanilide)-1,2-diaminoethane	171
83	Cr(III)	Potentiometer	Ion selective electrode	2.0×10^{-7} M	Electroplating wastewater samples	*tri-o*-Thymodite	172
84	Cr(III)	Potentiometer	Ion selective electrode	5.8×10^{-7} M	Electroplating wastewater samples	4-Amino-3-hydra zino-6-methyl-1,2,4 -triazin-5-one	173
85	Cr(III) Cr(VI)	Cathodic stripping voltametry	Microwave assisted digestion	2.9 μg L^{-1} or 1.0 ng m^{-3} for Cr(VI),	Urban air	-	174
86	Cr(III)	Potentiometer	Ion selective electrode	5.3×10^{-7} M	Urine and synthetic plasma, wastewater in electroplating industries	5-Amino-1-phenyl-1*H*-pyrazole-4-carboxamide	175
87	Cr(VI)	Voltammeter	Preconcentration	0.046 μmol L^{-1}	Industrial wastewater samples	Screen-printed carbon electrode modified with poly-l- histidine film	176
88	Cr(VI)	Square wave voltammeter	Electrode deposition	4.6 ppb	-	Pyridine-function alized sol–gel film	177
89	Cr(VI)	Differential pulse voltammeter	Electro chemical determination	8.5×10^{-7} M for silver and 4.0×10^{-7} M for gold nano particles	Tap water and Sea water samples	Carbon screen-printed electrodes with metal nanoparticles	178
90	Cr(VI)	Potentiometer	Solid state potentiometric sensors	9.0×10^{-7} M for carbon pastes, 6.3×10^{-7} M for graphite epoxy	River waters and leachates from municipal solid waste landfills	Carbon pastes and Graphie-epoxies modified with diphenylcarbazide	179
91	Cr(III)	Potentiometer	Membrane sensor	7.0×10^{-7} M (40 ppb)	Industrial waste water samples	*N*-(1-Thien-2-ylethylidene) benzene-1,2-diamine	180
92	Cr(VI)	Adsorptive stripping voltammeter	Adsorptive accumulation of complex	0.02 ppb (3.8×10^{-10} M)	Natural waters and effluents and ore samples	2,2'-bipyridine	181
93	Cr(VI)	Adsorptive stripping voltammeter	-	2 μg L^{-1}	Crude oil and sludge samples	Cu–Adenine complex	182
94	Cr(III)	Potentiometer	Electrochemical detection	7.9×10^{-7} M	Natural water samples	Modified carbon fiber electrode by *n*-hexyl calix [4] resorcinarene	183
95	Cr(VI)	Catalytic adsorptive stripping voltammeter	Electrochemical detection	0.19 nM	Natural water samples	Refreshable mercury film silver based electrode	184
96	Cr(III)	Differential pulse anodic stripping voltammeter	Electrochemical detection	2.0 μg L^{-1}	Tap water samples	Stannum film electrode	185
97	Cr(III) Cr(VI)	Adsorptive stripping voltammeter	mass-transport controlled preconcentration step	0.336 nM for Cr(VI) and 0.414 nM for total Cr	River water samples	Rotating-disc bismuth film electrode/diethylenetriami ne pentaacetic acid	186
98	Cr(VI)	Catalytic adsorptive stripping voltammeter	Adsorptive preconcentration	0.002 ng mL^{-1}	Food and wastewater samples	Hanging mercury drop electrode/rubeanic acid	187
99	Cr(VI)	Spectro - fluorometer	Fluorescence quenching	0.5 ng mL^{-1}	Synthetic samples	Terbium composite nanoparticles	188

S. No.	Analyte	Analytical Instrument used for the detection	Method	Limit of Detection (LOD)	Matrix	Supporting media	Ref
100	Cr(VI)	Spectro - fluorometer	Fluorescence quenching	0.01 μg mL^{-1}	Synthetic and wastewater samples	Luminescent and magnetic Fe_3O_4/pyrene/polyacrylamide	189
101	Cr(VI)	Spectro-fluorometer	Fluorescence quenching	0.8 ng mL^{-1}	Synthetic and wastewater samples	Terbium composite nanoparticles	190
102	Cr(VI)	Spectro-fluorometer	Oxidation of non-fluorescent rhodamine B hydra zide to fluorescent rhodamine B	5.5×10^{-9} M	Synthetic samples, drinking water and river water samples	Rhodamine B hydrazide	191
103	Cr(III) Cr(VI)	Spectro-fluorometer	Solvent extraction of fluorescent reagent	0.43 μg L^{-1} for Cr(VI)	Soil samples, tap and wastewater samples	Tetraphenylphosphonium bromide	192
104	Cr(VI)	Spectrophotometer	Sequential injection analysis	0.16 μg mL^{-1}	Alloy steels, sewage sludge and wastewater samples	Detection of a blue unstable intermediate compound resulting from the reaction of Cr(VI) with hydrogen peroxide (H_2O_2) in acidic medium	193
105	Cr(III) Cr(VI)	Spectro-fluorometer	Luminescence quenching	9.1×10^{-9} M for Cr(VI)	Natural water samples	Quercetin	194
106	Cr(VI)	Spectrophotometer	Biosorption	1.7 μg L^{-1}	Electoplating wastewater	Xanthated chitosan	195
107	Cr total	ICP-OES	Cloud point extraction	1.2 μg L^{-1} (LOQ)	Petroleum produced water samples	Triton X-114	196
108	Cr(VI) Cr(III)	ICP-OES	-	-	Electroplating wastewater, black tea and hot and black pepper	Silica MCM-41 modified with tetra azamacrocyclic compound	197
109	Cr(III)	ICP-OES	Solid-phase extraction	0.64 and 0.87 ng mL^{-1}	Biological materials and water samples	Silica gel-immobilized vanillin derivates	198
110	Cr total	ICP-OES	Complexation with ligands	0.31 μg L^{-1}	Tap water and natural water samples	*N*,*N*'-ethyl enebis (ethane sulfonamide)	199
111	Cr(III) Cr(VI)	ICP-AES	Ion exchange chromatography	0.050 mg L^{-1} for Cr(III) and 0.090 mg L^{-1} for Cr(VI)	Australian fly ash	-	200
112	Cr(III) Cr(VI)	ICP-AES	-	0.037 mg L^{-1} for Cr(VI)	Dying wastewater samples	-	201
113	Cr(III)	ICP-OES	Solid phase extraction	0.91 ng mL^{-1}	Pig liver and water samples	Zincon-modified activated carbon	202
114	Cr(III) Cr(VI)	ICP-MS	Solid phase extraction	4.43 pg $mL^{?1}$ for Cr(III)and 8.3 pg $mL^{?1}$ for Cr(VI)	Lake water, tap and well water samples	Cr(III)-imprinted silica gel	203
115	Cr(VI)	ICP-MS	Acid extraction	-	Ambient air samples	Mixed cellulose ester filters	204
116	Cr(III), Cr total	Chemiluminescence analyzer	Chemiluminescence	-	Natural water samples	Lucigenin-KIO_4	205
117	Cr(III)	Flow injection Chemiluminensce nce	Chemiluminescence		Real water samples	Luminol–H_2O_2	202
118	Cr(III), Cr total	Chemiluminescence analyzer	Chemiluminescence	1.6×10^{-16} mol L^{-1}	River water, mineral water, tap and drinking waters	Luminol–H_2O_2	206
119	Cr(VI)	Spectrophotometer	Chelation	-	Steels, alloys, water samples and synthetic mixtures	*bis*-(Salicylaldehyde) *ortho*-phenylenediamine	207
120	Cr(III) Cr(VI)	Spectrophotometer	Oxidation of the 2-amino-5-methyl phenol with H_2O_2	0.054-0.10 ng mL^{-1}	Natural and industrial wastewater	2-Amino-5-methylphenol with H_2O_2	208
121	Cr(VI)	Spectrophotometer	Chelation	-	Food samples	3,4-dihydroxy benz aldehydeisonicotinoyl hydrazone	209
122	Cr(VI)	Spectrophotometer	Solvent extraction	0.08 μg mL^{-1}	Tannery effluent, electroplating waste	Tribenzylamine	210
123	Cr(III) Cr(VI)	Spectrophotometer	Chelation	-	Tap water and mineral water samples	Chromo tropic acid	211
124	Cr(VI)	Spectrophotometer	Solvent extraction	-	Alloy samples, industrial wastewaters	2-Octylamino pyridine	212

S. No.	Analyte	Analytical Instrument used for the detection	Method	Limit of Detection (LOD)	Matrix	Supporting media	Ref
125	Cr(VI)	Spectrophotometer	Chelation	0.0217 μg mL^{-1}	Electroplating wastewater	Sodium diphenyl amine sulfonate	213
126	Cr(VI)	Spectrophotometer	Colourimetric	7.87 μg mL^{-1}	Lake water	2,2-Azino-*bis*-(3-ethylbenzo-thiazol ine-6-sulfonic acid) diammonium salt	214
127	Cr(III)	Spectrophotometer	Complexation	0.8 ng mL^{-1}	Tap water, river water and synthetic mixtures	α-benzoin oxime	215
128	Cr(VI)	Spectrophotometer	Solvent extraction	0.25 μg /25 mL	Synthetic mixtures, natural and electro plating wastewaters	Tetrabutylammonium-iodide	216
129	Cr(III) Cr(VI)	Spectrophotometer	Low pressure ion chromatography with flow injection spectro- photometric analysis	1.25 μg L^{-1} for Cr(VI) 3.76 μg L^{-1} for Cr(III)	Tannery wastewater samples	Diphenylcarbazide	217
130	Cr(VI)	Spectrophotometer	Sorption	-	Aqueous solutions	Quaternary amine groups (Lewatit MP 64 and Lewatit MP 500)	218
131	Cr(III) Cr(VI)	Spectrophotometer	Ultrasound-assisted cloud point extraction	12 ng mL^{-1}	Environmental water samples	Cetyltrimethylammonium bromide	219
132	Cr(VI)	Spectrophotometer	Adsorption	-	Aqueous solutions	Turkish brown coals	220
133	Cr(VI)	Spectrophotometer	Adsorption	-	Wastewater samples	Thiocarbamoyl chitosan	221

The pie chart (Fig. 2) shows the percentage of the papers described about the determination of chromium in various samples such as, natural waters, industrial effluents, biological samples (plant, soil), synthetic mixtures, food samples and ambient air samples. From the Fig. 2, over 40 % of the research papers were described about the determination of chromium in natural water samples. Around 25 % of the papers were described about the industrial effluents such as, industrial wastewater, electroplating effluents and tannery effluents. The literature survey clearly indicates that most researchers were concentrated on the determination of chromium in water samples, but in ambient air samples was not extensively studied due to difficulty in its measurement. It is observed that only around 4 % of the reviewed papers described about the determination of chromium in ambient air (Fig. 2). The determination of hexavalent chromium in ambient air is most important because it was included in carcinogenic list by the USEPA through inhalation route[5]. So, the future research has to concentrate on this issue to protect the human from cancer. Another important issue in chromium determination is the speciation studies. Hexavalent chromium is well known carcinogen whereas, trivalent chromium has biological importance. Some researchers[104-106,110,111,117,130] reported the concentration of total chromium in various environmental samples. The speciation study reveals the toxicity about the chromium presence in the specified matrix of the environment.

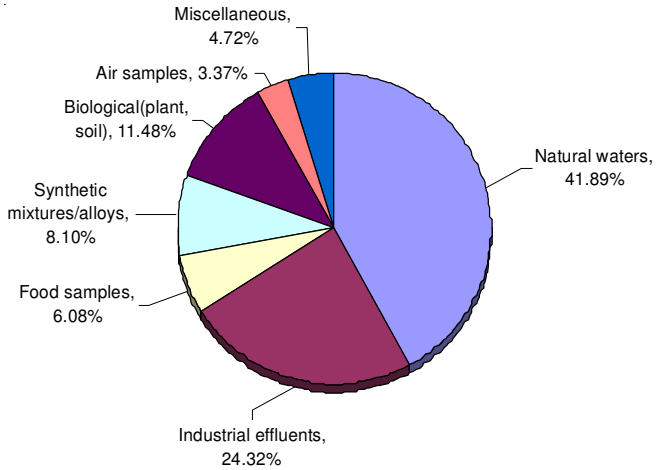

Fig. 2. Research papers published regarding the determination of chromium in various samples

We hope that the present review paper gives more information about chromium determination in environmental and biological samples with various analytical techniques and reveals the future important issues, such as speciation studies and the determination of hexavalent chromium in ambient air.

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