Research Article

ASSESSMENT OF CHROMIUM IN DRINKING WATER, SOIL AND INDUSTRIAL EFFLUENTS OF SANAND INDUSTRIAL AREA, GUJARAT

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A R T I C L E I N F O	A B S T R A C T
	A speciation analysis of chromium was done in water, soil and industrial effluents using two different analytical instruments. Correlating the results of Cr (VI) in soil obtained by FAAS and U.V.Visible Spectrophotometers gives the correlation coefficient as 0.9840. Although chromium loss was observed at the time of sample processing, no significant difference was observed when correlating the results obtained by sum of Cr (VI) and Cr (III) with that of total chromium in soil using FAAS (R2 = 0.9989). Accuracy of the method was validated by performing spiking. The spiking recoveries was between 91 – 106% and %RSD <5%.Furthermore, for comparison purposes five soil and water samples were collected apart from the industrial area of Sanand (residential areas) and their soil Cr (VI) levels are within the acceptable level of 10 mg/kg of soil as proposed by WHO.

INTRODUCTION

The French chemist Vauquelin discovered chromium (Cr) in Siberian red lead ore (crocoites) in 1798. As a transition element, chromium is located in the VI-B group of the periodic table having a ground state electronic configuration Ar $3d^5 4S^1$ (Shanker *et al.*, 2005). Chromium exhibits a wide range of possible oxidation states, where the +3 state is the most stable energetically; the +3 and +6 states are most commonly observed in chromium compounds(Samborska, Stepniewska and Stepniewski, 2004), whereas the +1, +4 and +5 states are rare (Świetlik, 1998) (Toxicology and Medicine, 2011). Chromium is the main component in the manufacture of steel, stainless steel, alloys, metal plating for prevention of corrosion, colouring agents for emerald green glass, chemical analysis, leather tanning, textile color pigments and mordents (Santonen, Zitting and Riihimäki, 2009) (U.S. Environmental Protection Agency, 2011) (Jacobs, Motzer and Abbott, 2004) (Santonen, Zitting and Riihimäki, 2009) (Toxicology and Medicine, 2011) (Fernández *et al.*, 2013). It is also a trace mineral essential to the nutrition of man and animals (Ishibashi, Cervantes and Silver, 1990)(Union, Pure and Chemistry, 1986) (Pechova and Pavlata, 2007).

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The toxic effects of hexavalent chromium have been proven to be a type one carcinogen by ASTDR (Toxicology and Medicine, 2011). Hexavalent chromium is thus dangerous to the workers working in steel, textile, and leather processing industries (Aitio *et al.*, 1984). It also causes allergic reactions such as skin rashes, nose irritations and nosebleeds. Major health problems due to high exposure to hexavalent chromium are lung cancer (respiratory problem), perforation of nasal septum, asthmatic bronchitis, bronchospasms, edema, weakened immune systems, kidney and liver damage, genetic alteration and death(Garg, Tripathi and Srinath, 2012) (Wise and Wise, 2012).

The most common heavy metals found at contaminated sites, with respect to scale of large quantity are Lead (Pb), Chromium (Cr), Arsenic (As), Zinc (Zn), Cadmium (Cd), Copper (Cu), Nickel (Ni) and Mercury (Hg). Chromium contamination in the environment is found to be very large because of rapidly increasing industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals etc. Chromium contamination in soil can increase risks and hazards to humans and the ecosystem by direct ingestion from contaminated soil, drinking of contaminated ground water, reduction in food quality via phytotoxicity, reduction in land usability for agricultural production causing food anxiety, and soil possession problems(Kuiper *et al.*, 2004). Breathing, eating,

drinking etc. are the various means by which human beings are exposed to chromium(Adeniji, 2004). Chromium contamination is mainly found in Air, water and soil. Water and soil contamination is mainly due to continuous discharge of industrial, domestic and agricultural wastes in rivers, lakes, and land (Khamis, Jumean and Abdo, 2009) (Sharma and Adholeya, 2011). Regular use of irrigation water contaminated with sewage or industrial effluents results in the high chromium levels in agricultural fields and crops(Amin *et al.*, 2013) (Stasinos and Zabetakis, 2013).

The Public Health Goal in California proposed the permissive limit for the level of hexavalent chromium in drinking water as 0.02 ppb(Adams and Alexeeff, 2011), which is the estimated "one in one million" lifetime cancer risk level. This means that for every million people who drink two litres of water with that level of hexavalent chromium daily for 70 years, no more than one person would be expected to develop cancer from exposure to hexavalent chromium. The "one-in-one million" risk level is widely accepted by doctors and scientists as the "negligible risk" standard (Environmental Protection agency, 2011) (Adams and Alexeeff, 2011). In this study, a speciation analysis of chromium was done on the samples that were collected from Sanand industrial area of Gujarat. In Gujarat, Sanand is a place having industries that are using and processing chromium. Drinking water, soil and industrial effluent samples were collected for chromium analysis. A correlation study was carried out to between two analytical instruments. Further we have also correlated the results obtained by different estimation methods and loss of chromium at the time of sample processing was calculated. To the best of our knowledge we are the first reporting the speciation of chromium in samples collected from the Sanand area of Gujarat, India.

MATERIALS AND METHOD

Instrumentation

A fully automated double beam flame atomic absorption spectrophotometer, Shimadzu AA-7000 was used in this study for the estimation of chromium. Spectrophotometric estimation was carried out by double beam U.V.Visible Spectrophotometer, Shimadzu UV-1800. A Direct Q Millipore system was used to obtain 18 mΩ deionized water for the preparation of standards, reagents and buffer solution. A highly sensitive weighing balance (AB265-S Mettler Toledo, USA) was used for the weighing of chemicals.

Materials

The materials used in this study and their sourcing were as follows

Total chromium standard solution for AAS traceable certified material from Sigma-Aldrich, product no. 02733. Chromium (VI) standard solution for Spectrophotometric analysis traceable certified material from Sigma-Aldrich, product no. 02673, CAS no. 7789-00-6. Ammonium pyrrolidinedithiocarbamate (APDC) from HiMedia, AR Grade, CAS no. 5108-96-3.Methyl isobutyl ketone (MIBK) from Fisher (Qualigens), AR Grade, CAS no. 108-10-1.Bromophenol blue indicator from SRL, AR Grade, CAS no. 115-39-9. Sodium hydroxide from Merck, GR Grade, CAS no. 1310-73-2.Sulfuric acid 98% from Merck, GR Grade, CAS no. 7664-93-9.1,5-diphenylcarbazide (DPC) from

Merck, AR Grade, CAS no. 140-22-7. Acetone from SRL, AR Grade CAS no. 67-64-1. Nitric acid 69% from Merck, GR Grade, CL3C630939. Sodium carbonate from Merck, AR Grade, CAS no. 497-19-8. Magnesium chloride from Merck, AR Grade, CAS no. 7791-18-6.K_2HPO_4 from Merck, AR Grade, CAS no. 7758-11-4.KH_2PO_4 from Merck, AR Grade, CAS no. 7778-77-0. Lead chromate from Merck, AR Grade, CAS no. 7758-97-6.Hydrogen peroxide 30% from Merck, AR Grade, CAS no. 7722-84-1.

Methods used in this study

Method 7196A (colorimetric method for hexavalent chromium)

This method was used to determine the concentration of dissolved hexavalent chromium in water. This method is applicable for the estimation of hexavalent chromium in domestic and industrial waste. It is used to analyze samples containing 0.5-50 mg/L Cr (VI).

Method 218.4 (Chelation Extraction method for hexavalent chromium)

This method is used to determine the concentration of dissolved hexavalent chromium in drinking and saline water. It is used to analyse samples containing 10 - 250 µg/L Cr (VI)

Method 3050 (Acid Digestion for soil)

The method digests solid samples and primarily moves metals into a soluble form for analysis on the Atomic Absorption Spectrophotometer. This method is mainly used to extract total chromium from soil.

Method 3060 A (Alkaline Digestion for Hexavalent chromium)

This method is used to digest soil samples for the extraction of hexavalent chromium in soil. Digestion of soil is carried out at highly alkaline pH.The extracted hexavalent chromium can be analysed using FAAS.

Sample collection

Fifteen soil and water samples were collected from the Sanand industrial area. Soil samples were collected from a depth of 15 to 20 cm. For comparison purposes, five soil and water samples were collected from the Sanand Residential areas. Soil samples were collected in plastic sample bags and water samples were collected in glass bottles that were washed with 10% Nitric acid and rinsed with Milli Q water before use it. Four industrial effluents were collected from the drainage lines of industrial area of Sanand were labelled as IES 1 to IES 4. 15 soil samples were labelled as San 1 to San 15 and 5 control soil samples were labelled as CS 1 to CS 5. Fifteen water samples were labelled as WS 1 to WS 15 and 5 control water samples were labelled as CWS 1 to CWS 5.

Sample processing

Extraction of total chromium from soil samples

For extraction of total chromium in soil, Acid digestion method (Method 3050) was employed. Under hot condition combinations of several acids such as Nitric acid and Hydrochloric acid followed by Hydrogen peroxide was used. Total chromium detection was carried out by flame Atomic Absorption Spectrophotometer.

Extraction of hexavalent chromium from soil and industrial effluent samples

Leaching of hexavalent chromium from soil and effluent was carried out by alkaline digestion method. Digestion solution was a combination of NaOH and Na_2CO_3 at pH 11.5 and plays an important role for extracting hexavalent chromium. Along with nitric acid, many in-organic salts such as magnesium chloride and lead chromate were used. To prevent change in pH, Phosphate buffer was used. Solution was filtered with 0.45 µm membrane filter. Samples were aspirated in flame atomic absorption spectrophotometer for the quantification of hexavalent chromium. Under acidic condition, hexavalent chromium gives purple colour complex with 1, 5- diphenylcarbazide and it can also be quantified at 540 nm using U.V.Visible spectrophotometer.

Trivalent chromium determination in soil residue

The soil residues obtained after leaching hexavalent chromium were treated with a combination of concentrated nitric and sulphuric acid with 30% hydrogen peroxide under hot condition which leads to the extraction of trivalent chromium. The solution was filtered with 0.45 µm membrane filter and was aspirated in FAAS for quantification.

Estimation of hexavalent chromium from drinking water samples

Ammonium pyrrolidinedithiocarbamate (APDC) and Methyl isobutyl ketone (MIBK) acts as a chelating agents for the extraction of hexavalent chromium from water samples. For quantitation of hexavalent chromium extract was aspirated in FAAS. This method was mainly applied to analyse samples containing 10 to 250 µg/L of Cr (VI).

RESULTS AND DISCUSSION

Calibration of Flame Atomic Absorption Spectrophotometer

The calibration of FAAS was done with the series of five chromium standards and their linear straight line standard graph was plotted and confirmed to the equation Y=0.9400x+4.0961 showed a good correlation coefficient R^2=0.9960. The various parameters for the experiment are described in Table 1.

Table 1 Instrumental parameters at the time of analysis in FAAS

Sr.no.	Parameters	Setting
1.	Wavelength	357.9 nm
2.	Lamp Current	7.0 mA
3.	Slit width	0.2 nm
4.	Flow rate of supporting gas (air)	15.0 L/min
5.	Flow rate of Fuel gas (acetylene)	2.8 L/min
6.	Burner Height	9 mm
7.	Burner Angle	0 degree
8.	Lamp Mode	BGC-D2

Calibration of U.V.Visible Spectrophotometer

The calibration of U.V.Visible Spectrophotometer was done with the series of four chromium standards and their linear straight line standard graph was plotted and was as per the equation Y=0.8932x+0.5778 showing a good correlation coefficient R^2=0.9996. The various U.V.Visible spectrophotometric parameters for the experiment are shown in Table 2.

Table 2 Instrumental Parameters at the time of analysis in U.V.Visible Spectrophotometer

Sr.no.	Parameters	Setting
1.	Measuring mode	Absorbance
2.	Slit width	1.0 nm
3.	Wavelength type	Point
4.	S/R Exchange	Normal
5.	Scan range	190 – 1100 nm
6.	Scan speed	medium
7.	Scan Pitch	Auto
8.	Rec. Range	0.0001 ~ 1.000 A

Total chromium concentration in soil samples

Extraction of total chromium in soil sample was carried out by acid digestion method EPA 3050. Results shows that the level of total chromium in soil collected from the industrial area was very high as compared to the control soil samples collected away from the industrial area of Sanand. Highest and lowest level of chromium in industrial soil sample was found to be 291.62 PPM (San 11) and 45.21 PPM (San 1). Following are the results of total chromium content in soil having %RSD <5% and after spiking with 100 ppm chromium spike recovery was obtained between 91% – 106%.

Table 3 Total chromium content in soil sample

Soil Samples	Mean ± SD (PPM)	% RSD	Spike Recovery
San 1	45.25 ± 1.6	3.69	95.85
San 2	47.26 ± 2.2	4.76	103.56
San 3	55.37 ± 1.3	2.47	98.55
San 4	94.77 ± 2.8	3.05	100.27
San 5	114.16 ± 2.7	2.44	102.35
San 6	86.95 ± 1.1	1.35	105.01
San 7	189.67 ± 2.8	1.49	95.01
San 8	220.62 ± 4.8	2.19	98.66
San 9	172.41 ± 3.1	1.83	102.86
San 10	204.56 ± 3.7	1.84	102.09
San 11	291.62 ± 3.7	1.29	104.91
San 12	165.53 ± 3.3	2.00	101.87
San 13	167.52 ± 4.1	2.46	96.02
San 14	144.61 ± 3.7	2.62	101.88
San 15	144.37 ± 3.1	2.20	98.05
CS 1	20.87 ± 2.2	1.80	101.25
CS 2	25.46 ± 2.1	2.56	103.63
CS 3	18.78 ± 2.6	1.75	99.54
CS 4	19.54 ± 1.4	1.69	94.86
CS 5	22.68 ± 1.9	2.13	92.51

Each soil samples were taken in triplicates and their results are plotted in terms of total chromium concentration as mean ± SD. Spike recovery of each sample was recorded by adding a known concentration of chromium and it is represented in terms of percentage.

Detection of hexavalent chromium level in soil samples

Extraction of hexavalent chromium in soil was carried out by alkaline digestion for hexavalent chromium (Method 3060A). This method is specific for the extraction of Cr (VI) from soils, sludge etc. After extraction of hexavalent chromium from soil, two techniques were employed for the estimation of Cr (VI) namely FAAS and U.V.Visible Spectrophotometer. In case of spectrophotometric analysis 1,5-diphenylcarbazide produces purple colour complex in the presence of Cr (VI) and it can be read at 540 nm against reagent blank. Highest and lowest levels of Cr (VI) was found in San 13 and San 1. The contamination level of Cr (VI) in San 5, 8, 9, 11, 13, 15 (FAAS results) were very high as compared to the control soil samples collected awayfrom the industrial area of Sanand. (Fig. 2) The level of Cr (VI) in control samples CS 1 to 5 and San 1, 2, 3, 4, 6, 7, 10, 12, 14 samples (FAAS results) were within

Table 4 Hexavalent chromium content in soil sample by two different analytical instruments

Soil Samples	FAAS Results			U.V.Visible Results		
	Mean ± SD (PPM)	% RSD	Spike Recovery	Mean ± SD (PPM)	% RSD	Spike Recovery
San 1	6.49 ± 0.2	4.52	95.35	5.51 ± 0.2	4.71	94.21
San 2	5.52 ± 0.2	4.20	99.01	4.30 ± 0.1	4.41	94.60
San 3	6.75 ± 0.3	4.50	101.34	5.53 ± 0.2	4.38	99.62
San 4	8.89 ± 0.3	3.99	98.03	7.29 ± 0.3	4.75	104.62
San 5	11.49 ± 0.3	2.77	96.95	10.70 ± 0.4	3.98	101.25
San 6	7.7 ± 0.3	4.30	100.88	6.19 ± 0.1	1.51	92.51
San 7	9.5 ± 0.3	3.79	98.02	8.78 ± 0.2	2.69	96.54
San 8	12.22 ± 0.1	1.31	104.41	10.65 ± 0.3	3.45	99.23
San 9	11 ± 0.5	4.72	103.66	11.41 ± 0.3	3.32	102.32
San 10	9.88 ± 0.4	4.07	101.15	8.68 ± 0.2	3.40	100.25
San 11	13.62 ± 0.5	3.83	98.25	11.91 ± 0.3	2.88	98.24
San 12	8.67 ± 0.3	4.60	101.62	6.93 ± 0.2	3.99	97.62
San 13	11.64 ± 0.3	3.17	102.53	9.51 ± 0.2	3.15	94.16
San 14	9.55 ± 0.3	3.78	97.64	7.71 ± 0.3	4.27	93.97
San 15	10.42 ± 0.4	3.89	98.65	9.62 ± 0.1	1.30	103.58
CS 1	4.21 ± 0.2	3.45	99.74	3.98 ± 0.2	2.14	99.54
CS 2	5.2 ± 0.4	2.85	102.84	4.37 ± 0.1	2.68	102.41
CS 3	3.37 ± 0.3	3.39	104.64	2.21 ± 0.2	3.23	98.74
CS 4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
CS 5	5.2 ± 0.4	2.98	95.62	4.89 ± 0.3	2.89	99.51

The above table shows the comparison of results of chromium estimation by two different analytical instruments. Each soil samples were taken in triplicates and their results were plotted in terms of mean ± SD. Spike recovery of each sample was recorded by adding known concentration of chromium and it is represented as percentage.

Table 5 Trivalent chromium content in soil samples

Soil Samples	Mean ± SD (PPM)	% RSD	Spike Recovery
San 1	26.18 ± 1.0	4.17	101.01
San 2	28.89 ± 1.2	4.43	98.15
San 3	39.47 ± 1.3	3.44	102.20
San 4	74.86 ± 2.6	3.57	101.36
San 5	93.48 ± 2.7	2.91	98.98
San 6	66.63 ± 1.4	2.18	101.61
San 7	166.89 ± 2.9	1.79	98.62
San 8	194.61 ± 3.2	1.65	104.96
San 9	155.82 ± 1.2	0.79	97.85
San 10	184.31 ± 1.3	0.74	102.20
San 11	267.38 ± 2.6	0.98	103.22
San 12	146.98 ± 2.5	1.74	97.38
San 13	145.95 ± 3.2	2.21	101.23
San 14	123.91 ± 1.4	1.21	104.89
San 15	126.46 ± 1.7	1.35	97.37
CS 1	14.29 ± 2.4	1.89	102.54
CS 2	19.61 ± 1.4	2.12	101.87
CS 3	12.87 ± 1.9	1.45	99.54
CS 4	17.88 ± 2.1	1.87	94.51
CS 5	16.58 ± 2.4	2.69	98.14

The above table shows each soil samples were taken in triplicates and their results are plotted in terms of mean ± SD. Spike recovery of each sample was recorded by adding known concentration of chromium and it is represented in terms of percentage.

the acceptable level 10 ppm as suggested by WHO. Furthermore, the correlation graph which was plotted (Fig. 1) between the results of Cr(VI) obtained by FAAS and U.V.Visible Spectrophotometer gave a regression equation as $y = 0.965x + 1.518$ and its correlation coefficient was $R^2 = 0.984$. EPA method 3050 was applied to the analysis of Cr (VI) by FAAS and was compared with the spectrometric method. Statistical results showed that there is no significant difference at 95% confidence level. For method accuracy check, soil samples were spiked with 50 ppm of Cr (VI) showing spike recovery between 91% - 105% and percent relative standard deviation less than 5%. The limit of detection for AAS was checked based on three times the standard deviation of blank (n=5) and was found to be 4 ppb. Table 4 shows the results of % RSD and Spiking recovery of Cr (VI) in soil and control samples by FAAS and U.V.Visible Spectrophotometer.

Assessment of trivalent chromium in soil samples by FAAS

The trivalent chromium estimation was done after extracting hexavalent chromium from soil by alkaline digestion method.

Table 6 Chromium speciation analysis results by FAAS

Soil Samples	Cr VI (PPM)	Cr III (PPM)	Cr VI + III (PPM)	Total Cr (PPM)	Unestimated Cr %
San 1	6.50	26.18	32.68	45.24	27.78
San 2	5.52	28.89	34.42	47.27	27.19
San 3	6.75	39.48	46.23	55.37	16.52
San 4	8.90	74.86	83.76	94.77	11.62
San 5	11.50	93.48	104.98	114.17	8.05
San 6	7.70	66.63	74.33	86.95	14.51
San 7	9.51	166.89	176.40	189.67	7.00
San 8	12.23	194.61	206.84	220.63	6.25
San 9	11.01	155.83	166.84	172.42	3.24
San 10	9.89	184.32	194.21	204.56	5.06
San 11	13.62	267.38	281.01	291.63	3.64
San 12	8.67	146.99	155.66	165.53	5.96
San 13	11.65	145.96	157.61	167.52	5.92
San 14	9.55	123.92	133.47	144.60	7.70
San 15	10.43	126.47	136.90	144.37	5.18
Control san 1	4.21	14.29	18.50	20.87	11.36
Control san 2	5.20	19.61	24.81	25.46	2.55
Control san 3	3.37	12.87	16.24	18.78	13.53
Control san 4	N.D.	17.88	17.88	19.54	8.50
Control san 5	5.2	16.58	21.78	22.68	3.97

Above table shows overall data of chromium speciation analysis. Loss of chromium at the time of processing of samples for speciation analysis was observed and is represented in terms of percentage.

Cr (III) level in industrial soil samples were compared with the control soil samples collected away from the industrial area of Sanand. Table 5 shows the results of % RSD and Spiking recovery of Cr (III) in soil and control samples. Soil samples spiked with 100 ppm standard chromium solution showed spike recovery between 94% – 105% and their percent relative standard deviation was less that 5%.
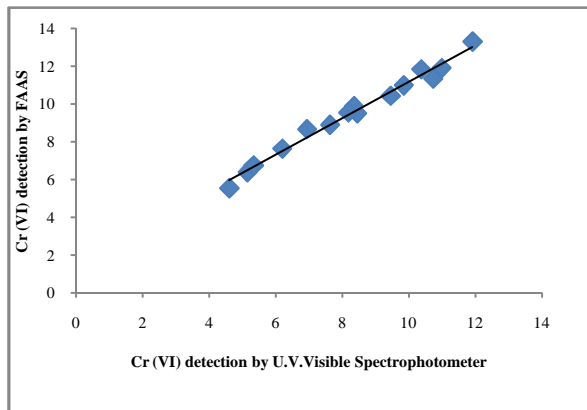

Figure 1 Correlation graph shows the results of Cr (VI) by FAAS and U.V.Visible Spectrophotometer. The linear correlation between the chromium estimation results of AAS and U.V.Visible spectrophotometer are represented in the figure above.
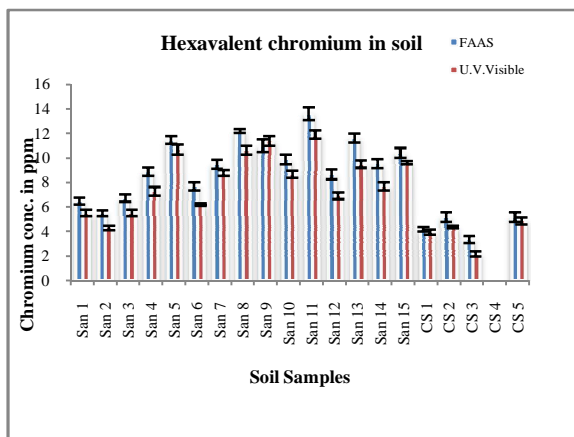
Figure 2 Graphical representation of the level of hexavalent chromium estimated by FAAS and U.V.Visible spectrophotometer. Above graph shows the level of hexavalent chromium as mean ± SD in industrial and residential soil samples by two different analytical instruments.
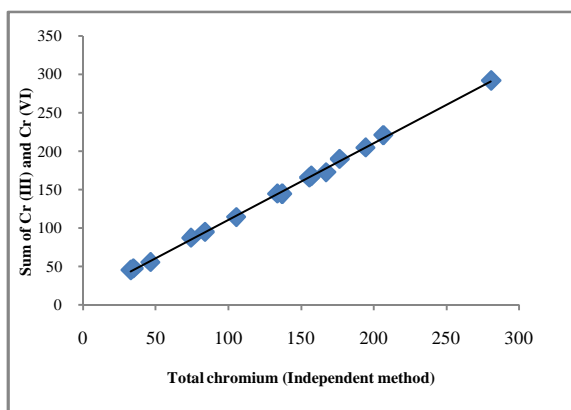

Figure 3 Correlation graph of results of total chromium (independent method) with the results of sum of Cr (VI) and Cr (III). This correlation is the result of 15 soil samples by two different methods.
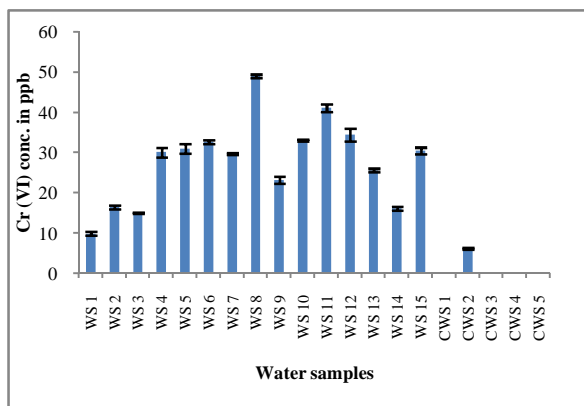

Figure 4 Graphical representation of values of hexavalent chromium in water samples by FAAS. Samples were taken in triplicates and their values were plotted in terms of mean ± SD. except CWS 2, the level of chromium in control soil samples was below detection limit.
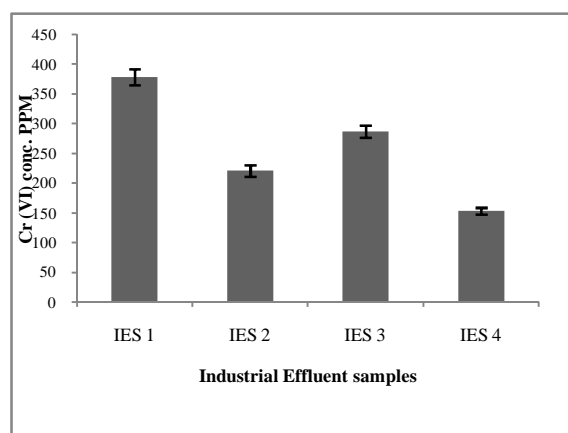

Figure 5 Graphical representation of values of hexavalent chromium in industrial effluent samples by FAAS. Levels of hexavalent chromium in effluent samples were reported as mean ± SD.

Speciation of chromium in soil samples by FAAS

Table 6 shows the speciation analysis of chromium by Atomic Absorption Spectrophotometer. Independent estimation of hexavalent, trivalent and total chromium was done by their specific methods. Comparing the values of total chromium with the values of Cr (VI) + Cr III shows the values of un-estimated chromium or chromium loss at the time of processing of sample for speciation analysis. Correlating the values of chromium obtained by sum of Cr (VI) and Cr (III) with total chromium values shows the regression equation $y = 0.9975x + 10.9983$ and its correlation coefficient $R^2 = 0.9989$. (fig. 3) Student t test was employed between the values of total chromium and the values of sum of Cr (VI) and Cr (III) and showed the data was significant at 95% confidence level and $p < 0.0001$.

Determination of hexavalent chromium in drinking water samples by FAAS

Ammonium pyrrolidinedithiocarbamate (APDC) and Methyl isobutyl ketone (MIBK) act as chelating agents for the extraction of Cr (VI) from water samples. This method was used to analyse the water samples containing the level of Cr (VI) from 10 to 250 ppm. Water samples were collected from different bore wells of industrial area of Sanand. For comparison purpose control water samples were collected away from the industrial area of Sanand. After processing of

water samples with method 218.4, water samples were spiked with 50 ppb of Cr (VI) for proper estimation of Cr (VI) using FAAS. (Fig. 4) It was found that all water samples and control 2 showed the level of Cr (VI) was very high as compared to the permissive limit suggested by PHG California.

Determination of hexavalent chromium in industrial effluents by FAAS

Effluent samples were collected from four different drainage lines of the industrial area of Sanand. The results shows that Cr (VI) in industrial effluent (Fig. 5) was very high and probably leads to soil and water contamination in nearby areas.

CONCLUSION

Sanand soil samples were processed with standard methods for speciation analysis of chromium in soils. In this study, hexavalent chromium detection was carried out by two analytical methods. A correlation graph was drawn between the results obtained by FAAS and U.V.Visible Spectrophotometer showing a good correlation coefficient R^2 = 0.984. Besides, statistical evaluation of data reveals that there is no significant difference between the two methods at 95% confidence level suggesting both the method were applicable for the determination of Cr (VI) from soil samples. Soil samples were compared with control soil samples collected away from the industrial area of Sanand. The levels of Cr (VI) in control soil samples were within the proposed limit suggested by WHO. Six soil samples show very high level of Cr (VI) as compared to the permissible limits. Similarly, a correlation graph was plotted between the values of total chromium (Independent method) in soil with the values of sum Cr (VI) and Cr (III) showing a regression equation $y = 0.9975x + 10.9983$ and a correlation coefficient R^2 = 0.9989. Student t test was employed between the values of total chromium with the values of sum of Cr (VI) and Cr (III) showing the data was statistically significant at 95% confidence level and $p < 0.0001$.

All these methods were evaluated using spiking method (adding known concentration of chromium) and satisfactory results were obtained having spiking recoveries between 91-106% and percent relative standard deviation less than 5%. Furthermore, water samples collected from industrial area and control water samples collected away from the industrial area were processed with standard method for Cr (VI) chelation, data reveals that the level of Cr (VI) in water samples from industrial area and control sample number 2 shows very high level of Cr (VI) in comparison with PHG. From drainage pipe lines, industrial effluents were also collected to check the level of chromium contamination.The main reasons for the contamination of ground water and soil are maybe due to the release of untreated effluents by industries.

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