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Short communication

Determination of hexavalent chromium by on-line dialysis ion chromatography in a matrix of strong colourants and trivalent chromium

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Abstract

Hexavalent chromium detection in the presence of a high load of colourants without any false positive and in-procedure oxidation of Cr(III) is an important area of study. Colourants are a class of interfering substances in many spectroscopic analyses and chromatographic separations and detection. A purification method using an on-line dialysis technique for ion chromatography (IC) has been developed to remove water-soluble anionic dyes and particulate colourants and other substances to facilitate Cr(VI) quantification and the method is discussed. The dialysis was optimized with Cr(VI) standard solutions for quantification. The efficacy of the procedure for the removal of anionic dyes and detection of Cr(VI) was checked with a Cr(VI) spiked synthetic preparation containing a water-soluble dye and trivalent chromium. Soluble Cr(VI) extracted with organic dyes from environmental samples was analyzed. The method has a detection limit of 5 μg/l, recovery rate of 100% and analysis time less than 20 min.

Keywords: Dialysis; Chromium

1. Introduction

Hexavalent chromium is a high priority pollutant and has been identified as a carcinogen to be monitored in the environment [1–3]. Hexavalent chromium monitoring has become inevitable in drinking water, wastewater, soil and even in air in some workplaces like stainless steel welding, spray-painting, abrasive blasting, etc. [4,5]. Several industrial coloured products like textiles, leather garments, shoes, toys, etc., have been identified for potential Cr(VI) pollution and are now subjected to screening. A great challenge exists in hexavalent chromium detection in cases of wastewater and solid wastes rich in organics including high amount of colourants, Cr(III), etc. Some of the colourants are particulate, while others are water-soluble and the latter are of more concern in the analysis. The soluble colourants like organic anionic dyes interfere seriously in the widely employed photometric method, which involves complexation of Cr(VI) with 1,5-diphenyl carbazide [6,7]. As any digestion meth-

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od is likely to turn Cr(III) to the Cr(VI) state, it is not possible to make any conventional approach for the destruction of organics. Wastewater collected from industries pertaining to dyes, chemicals, textiles, tanneries and printing inks, constitute such matrices. Jambunathan and Dasgupta studied a very similar problem earlier but which involved finished leather sample extracts [8] but the method was not an on-line purification technique and also was limited to dyes which could be bleached with chlorine. Ion chromatographic (IC) analysis with post column derivatization using diphenyl carbazide (DPC) was successfully used for hexavalent chromium detection in wastewater [9]. Several official procedures recommend IC analysis for Cr(VI) in the presence of Cr(III), e.g. ASTM [10], EPA [11] and NIOSH [12]. Although the IC technique is well accepted, wastewater samples with a high content of colourants (water-soluble organic anionic dyes and also particulates) cause serious noise affecting sensitivity and peak shapes. Water-soluble dyes also impair the columns irreversibly at times. Hence a good sample purification technique before ion chromatographic separation becomes necessary and on-line dialysis is found to be best for analyzing various environmental samples directly by IC. On-line dialysis for liquid chromatography was successfully applied to several biological, food and drug samples in earlier studies [13]. The present study is based on this technique and has been used for environmental samples, which have not been explored thoroughly. The method is very simple, reproducible, sensitive and reliable. Recovery studies were done with standard Cr(VI) and reported.

1.1. Significance of dialysis for this matrix

Most of the water-soluble dyes found in these samples were organic anionic dyes with some variation in chemistry. The relative transport efficiency of Cr(VI) versus organic anionic dye across the membrane is an important factor in the dialysis method. Kuban and Karlberg [14] have shown that the transport efficiency or diffusion rate of small inorganic ions are several orders greater than the transport efficiency of larger organic anions. With reference to Fick's law, the diffusion rate $J = -D(A/\tau)(\mathrm{d}c/\mathrm{d}x)$, and J of an analyte depends on its diffusion coefficient D (m^2/s), on the concentration gradient $-\mathrm{d}c/\mathrm{d}x$ (mol/m^4) and the effective membrane area A (m^2). The factor τ, the tortuosity of the membrane, is a constant including all relevant membrane parameters such as porosity, pore size, membrane thickness, etc. The diffusion coefficient D is expressed by the Stokes–Einstein relationship $D = kT/6\pi\eta r$ where k is the Boltzmann constant (J/K), T is absolute temperature (K),η the viscosity (kg m^{-1} s^{-1}) and r the radius of the analyte molecule. The diffusion rate at constant T and η depends entirely on the analyte diameter. This is the basis of employment of dialysis for analyzing Cr(VI) while removing soluble organic anionic dyes in this matrix.

2. Experimental

2.1. Instrumentation

The ion chromatograph was from Metrohm Ltd., Herisau, Switzerland. It consists of a Metrohm Model 709 IC pump (PEEK material of construction) and Metrohm model 733 IC separation center equipped with a Valco injector (Valco, Houston, TX, USA) fitted with 100- and 20-μl loops. The 100-μl loop is used for sample injection. The entire system is PEEK lined. Metrohm's Dialysis unit is the model 754, which consists of a dual channel peristaltic pump and a Plexiglas dialysis cell of volume 240 μl and 47 mm diameter. Cellulose acetate membrane of 0.20 μm pore size, 47 mm diameter and 115 μm thickness used for dialysis was also from Metrohm. IC Metro Data Software, version 1.44 was used to process all data. the photometric detection system was a Lambda 1010 from Bischoff, Leonberg, Germany. CETAC IC sep AN1 CART KIT, anion IC column (P/N: ANX-99-8511) is PEEK walled from Cetac Technologies, NE, USA. The RDR-1 Reagent Delivery/Reaction module from Timberline Instruments, Colorado, USA was used for post-column derivatization. The comparative photometric analysis was done using a Lambda 14 model UV–Vis spectrophotometer from Perkin-Elmer (Norwalk, CT, USA).

2.2. Reagents

1,5-Diphenyl carbazide GR was from Merck (Darmstadt, Germany); ammonium hydroxide, phosphoric acid, ammonium sulphate, dipotassium hydrogen orthophosphate, and sulphuric acid reagents of analytical grade and methanol of HPLC grade were procured from Merck (India). A blue shade water-soluble dye (Acid Blue 113) Colour Index No. [26360] manufactured by Indian Dyestuffs Industries Ltd. (Mumbai, India) was used. Basic chromium sulphate, technical grade was procured from Golden Chemicals Ltd. (Mumbai, India). HPLC grade water of 18.0 MΩ cm used for the preparation of mobile phase buffer and for other purposes in the procedure was prepared using an Elgastat Maxima model from Elgastat (Bucks, UK). Dipotassium hydrogen orthophosphate buffer of 0.13 *M* at pH 8.0 was used for extraction or dilution of environmental samples. The mobile phase was 25 m*M* ammonium sulphate prepared by dissolving 3.3 g of ammonium sulphate and 620 μl of ammonium hydroxide in 1 litre HPLC grade water. The post-column reagent was prepared by dissolving 0.5 g 1,5-diphenyl carbazide in 100 ml HPLC grade methanol and 25 ml of sulphuric acid and made up to 1 litre with HPLC grade water. The post-column reaction was effected by maintaining a pressure difference of 20 p.s.i. between the mobile phase and that of nitrogen gas (flow-rate of the reagent was 0.4 ml/min). Cr(VI) standard stock solution was prepared using potassium dichromate (GR label), certified reference of ACS, ISO purity from Merck (Darmstadt, Germany) and other standard solutions were prepared from the stock solution on the day of use.

2.3. Experiment

2.3.1. Sample preparation

Samples of wastewater and wet solid wastes were collected from an industrial effluent collection point in an industrial zone consisting of chemicals, dyes, tanning and textile industries (about 25 km south of Chennai, India with an average density of 5 units per km). Polyethylene sample bottles previously cleaned, rinsed with 1.0% nitric acid and further rinsed several times with pH 8.0 phosphate buffer were used for extraction. The samples collected were immediately purged with argon gas, sealed air tight and taken up for analysis within 3–4 h of collection. Slightly basic buffers are suitable for stabilizing Cr(VI) in aqueous solutions and normally phosphate buffer is used to quantify soluble Cr(VI) [15,16]. The official analytical procedures, namely DIN 53314 and EN420 followed in the leather and textile industries, require extraction with phosphate buffer of pH 8.0 and hence this was chosen to prepare samples. In this way, Cr(III) ions are mostly eliminated by precipitation but water-soluble organics mainly dyes could not be removed. In the case of analysis of wet-solid waste, sample preparation involved weighing 2 g in a 200-ml stoppered glass container with the addition of 100 ml of phosphate buffer at pH 8.0. The contents were then blanketed under argon and extracted thoroughly in a shaker at 50 rpm for 3 h. Most of the samples were so strongly coloured that a dilution was found necessary. A correct guideline for the dilution of a sample is drawn from the absorption coefficient of samples determined by spectrophotometry. When the absorption coefficient values exceed 0.5, dilution was necessary. In the case of liquid samples, sample preparation involved dilution to the extent of 10% by volume and pH adjustment to 8.0 with 1 *M* phosphoric acid or 1 *M* sodium hydroxide. The diluted liquid and extracted solid samples were centrifuged at 10 000 rpm for 10 min and then filtered through pleated Whatman 42 filter paper. The clear extracts were subjected to on-line dialysis–ion chromatographic analysis. Ion chromatographic analysis of Cr(VI) was carried out with an anion-exchange [17,18] column. The elution was done at a mobile phase flow-rate of 0.8 ml/min followed by on-line post-column derivatization with 1,5-diphenyl carbazide reagent filled into the post-column reactor and monitoring at 520 nm using a photometric detector.

2.3.2. Preparation of synthetic matrix

To validate this methodology for the kind of matrix elements particularly for colourants, a synthetic wastewater was prepared containing an organic anionic dye and Cr(III). Since wastewaters from tanning, dyes, and pigment industries are mixed, a high load of Cr(III) was included in the matrix at a level of 1000 μg/l. Cr(III) sourced from basic chromium sulphate was checked for its purity and

incorporated in the synthetic mixture which also checks this analytical approach for any in-procedure oxidation. Water-soluble organic anionic dye (Acid Blue 113) containing sulphonic functionality was chosen because its chemistry represents the frequently encountered cases. It was prepared at a concentration of 4% as in wastewater samples. The synthetic mixture of the dye and Cr(III) was prepared in sufficient quantity using the same phosphate buffer and four portions of 100-ml solutions were taken for analysis. One 100-ml portion was reserved as a blank, and each of the other three 100-ml solutions was spiked with Cr(VI) in the concentration range 20, 50 and 100 μg/l, respectively. The samples were centrifuged and analyzed by the proposed dialysis IC method.

2.4. Sample preparation by dialysis

The theory of on-line dialysis with a liquid chromatographic system has been described in the literature [19,20]. The on-line dialysis unit for ion chromatography consists of a dual channel peristaltic pump for conveying the sample and acceptor solutions and actual dialysis cell. In the dialysis cell, the ions from the flowing sample solution are built up to a maximum (an equilibration to the level of donor) in the stagnant acceptor, which is just very pure water of HPLC grade. The ions (collected in the acceptor) are then injected directly into the IC system. It is possible to optimize the dialysis conditions to match direct injection and also facilitate effective calibration with external standards. The equipment used for dialysis is exactly the same and its method of operation along with the quantities as described earlier by Buldini et al. [21]. Dialysis of samples was carried out using two valves, valve A fitted with a 100-μl loop and valve B fitted with a 20-μl loop. The dialysis membrane was conditioned by immersing the membrane in a Petri dish containing HPLC grade water for 2 min, until it was completely saturated with water. The procedure for dialysis is described in Table 1. For the final analysis by dialysis IC, the standard solutions of Cr(VI) were prepared in phosphate buffer of the same ionic strength and pH as that used for the sample extraction. Hence the donor was at pH 8.0 and the acceptor employed was only pure, HPLC-grade water.

3. Results and discussion

3.1. Optimization of dialysis with standard solutions of Cr(VI)

The first step in optimizing the dialysis was to find the transfer time, i.e. the time allowed for transferring the concentrated (with ions to the equilibrium) acceptor solution to the sample loop. The next step was to vary the time of dialysis from 3 to 15 min and finding the time at which the peak areas of the concentration measured with dialysis and direct injection agree. The dialysis is then said to be optimized. The donor flow-rate was varied from 0.3 to 0.6 ml/min and at least 0.5 ml/min was found necessary to produce the maximum area. A standard solution of Cr(VI) 100 μg/l concentration prepared in phosphate buffer pH 8.0 was used to harmonize the IC analysis with and without dialyses. The

Table 1
Dialysis program

Time (min)	Valve A	Valve B	Event
0–1.9	Fill	Inject	Rinsing of acceptor and sample channels and sample loop
2.0–12.0	Fill	Fill	Dialysis with stopped flow—when sample is dialyzed with stagnant acceptor
12.0–12.7	Fill	Inject	Transfer to sample loop—the acceptor solution concentrated with ions (equilibrium) from the sample is transferred to the sample loop
12.7	Inject	Inject	The acceptor solution concentrated with ions (to equilibrium) is injected into IC

transfer time had been varied in terms of 0.1-min increments and was optimized at 0.7 min. The dialysis depends on the total ion concentration. Complete agreement of the peak areas of the Cr(VI) from direct injection with that through dialysis was shown at 10 min. Similarly standard solutions of Cr(VI) of 50 and 20 μg/l were also studied and the recoveries with respect to their direct injections were found to be excellent. Optimization of the dialysis time for Cr(VI) recovery is plotted in Fig. 1 for three different levels studied: 20, 50 and 100 μg/l. The overlay of chromatograms of Cr(VI) of 100 μg/l obtained from: (a) direct injection and (b) dialysis mode of 10-min duration is shown in Fig. 2 to confirm optimum dialysis conditions. The dialysis time set is valid as long as the nature of membrane, thickness and the depth of the donor channel are kept the same [13]. The optimized dialysis condition was verified for a concentration down to 5 μg/l of Cr(VI).

3.2. Agreement of the dialysed sample injection and the direct injection

From the match of the peak areas of the direct injection of Cr(VI) reference solution with the dialysed injection (Fig. 2), it is concluded that a dialysis time of 10 min is adequate to match the

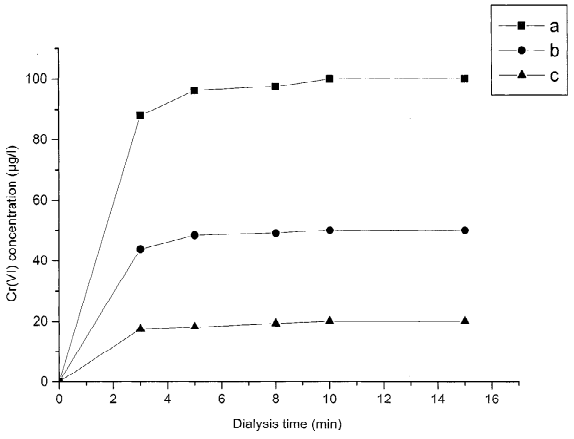

Fig. 1. Optimization of dialysis time for recovery of Cr(VI) with direct injection using standard solutions of Cr(VI) of different concentrations: (a) The full recovery of the 100 μg/l level is shown in 10 min dialysis time and is similar for all levels; (b) 50 μg/l; (c) 20 μg/l.

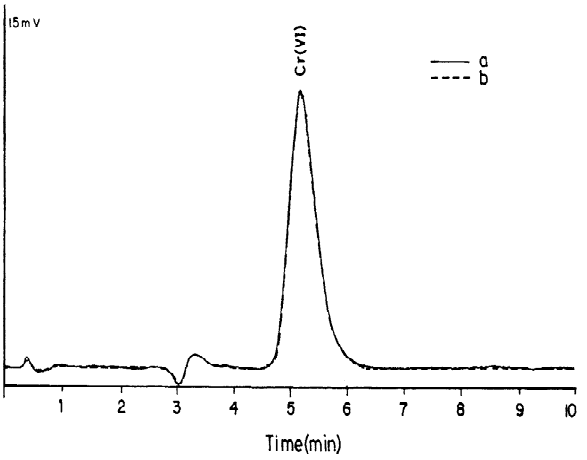

Fig. 2. Overlay of chromatograms of Cr(VI) reference solution of 100 μg/l concentration obtained by (a) direct injection; (b) dialyzed (optimized method) injection.

sampling techniques in terms of quantity of analyte transferred. In an earlier work, complete recovery of several anions by on-line dialysis technique was reported by Buldini et al. [21]. The donor solution (sample) was pumped at a flow-rate of 0.5 ml/min and at this flow-rate in 10 min, 5.0 ml of the sample would pass through the membrane. For instance if 100 μg/l solution of Cr(VI) was employed for dialysis and of the total 0.5 μg of Cr(VI) available in 5 ml passing through the membrane in that time, 0.024 μg is transferred into 240 μl stagnant acceptor. This is about 4.8% of the ions present in the donor solution subjected to dialysis and this level of concentration of Cr(VI) namely 0.024 μg/240 μl is the same as 100 μg/l of the original liquid. Hence the amount of ions injected by dialysis mode is said to match the direct injection.

3.3. Role of phosphate buffer

To study the role of the phosphate buffer, Cr(VI) standard solutions of 50 and 100 μg/l were prepared separately in water and phosphate buffer. On comparative analysis, it was found that the Cr(VI) values of aqueous preparations were lower, viz 39 and 74 μg/l as against 50 and 100 μg/l obtained for the corresponding preparations in phosphate buffer. Hence full recovery of Cr(VI) was achieved in phosphate buffer in 10 min of dialysis. This is due to

a good concentration gradient set by the phosphate buffer and thereby facilitating better Cr(VI) migration to the acceptor. However when the buffer strength was varied from 10 to 200 m*M*, there was no change in the result, either in the Cr(VI) concentration or its dependence on dialysis time.

3.4. Elimination of dye molecules

Wastewater samples of different colours like brown, blue, pink, red and indigo were chosen. These samples were found to contain dissolved organic anionic dyes. The dye removal studies were done by analyzing these extracts individually by direct injection and by dialysis. The same 10-min dialysis was followed because of the interest to find the elimination level of dye within the recovery time of Cr(VI). The analyses were carried out in flow-injection mode (without column in place) and without post-column derivatization but with detection made at the same 520 nm. The dialysis wastes of the respective extracts were also collected and analysed similarly but only by direct injections. The removal of dyes was in the range 86–98%, as inferred from the peak areas of different dye-containing extracts, produced by direct injections and dialyzed injections. The peaks from the flow-injection mode of one of the coloured wastewaters (without derivatization) and its drastic reduction after dialysis are shown in Fig. 3. This clearly indicates the extent of dye removal. The dye removal (with respect to the original dye level detected by direct injection) on varying dialysis duration was studied using a sample extract containing a soluble organic anionic dye (pink). This study also was done without the column in place and without post-column derivatization but with detection at 520 nm and the data are given in Table 2. The diffusion kinetics is believed to be the main reason for the slow transfer of organic anionic dye molecules and rapid transfer of Cr(VI) ions, and their relative transport efficiency is found to be 40 and 100%, respectively.

3.5. Method validation by a synthetic matrix

Different levels of Cr(VI) spiked to the synthetic preparation gave values which were in good agreement with similar concentrations analyzed in the absence of the matrix, i.e. 20.8 for 20 μg/l, 49.6 for 50 μg/l and 99.8 for 100 μg/l. The blank run of the matrix produced no signal for Cr(VI). The representative chromatograms of synthetic mixture spiked with Cr(VI), 20 μg/l injected with and without dialyses (by direct injection) are shown in Fig. 4 to prove the efficacy of dialysis.

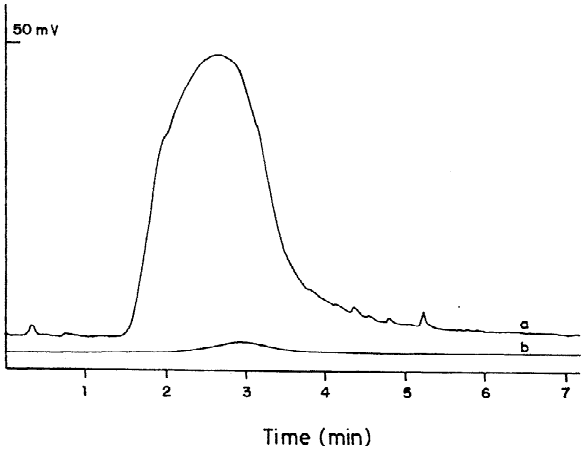

Fig. 3. Peaks of a dye (red) in coloured wastewater sample detected at 520 nm obtained in flow-injection mode without column and post-column derivatization; (a) By direct injection which shows the original level of dye; (b) By dialysis method (optimized) which shows the significant level of elimination of dye.

3.6. Analysis of real samples

Wastewater and wet solid waste having a high load of colourants were sampled freshly and prepared for the on-line dialysis IC analysis as described in Section 2.3.1. The results of some real samples showed the presence of Cr(VI), which was quantified

Table 2
Extent (%) of water-soluble organic anionic dye removal by dialysis is shown at different dialysis times

Dialysis time (min)	Extent of dye removal with respect to direct injection (regarded as 100%)
2	96.4
5	96.1
8	95.9
10	95.4
15	92.7

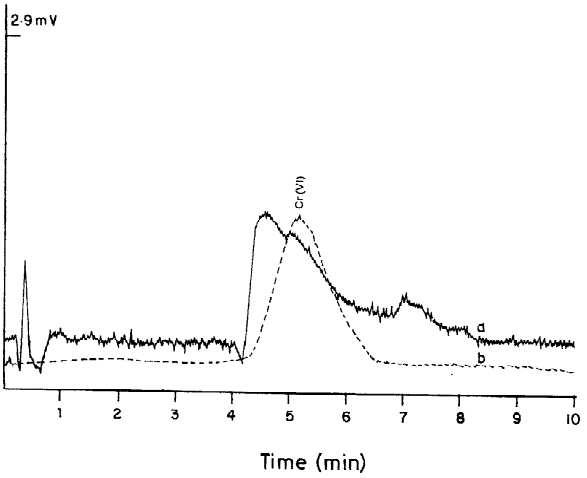

Fig. 4. Chromatograms of a synthetic mixture containing a dye, Cr(III) and Cr(VI) (at 20 μg/l). (a) Run without dialysis showing noise with dye and Cr(VI) remains unresolved. (b) Run with on-line dialysis (optimized method) showing only Cr(VI).

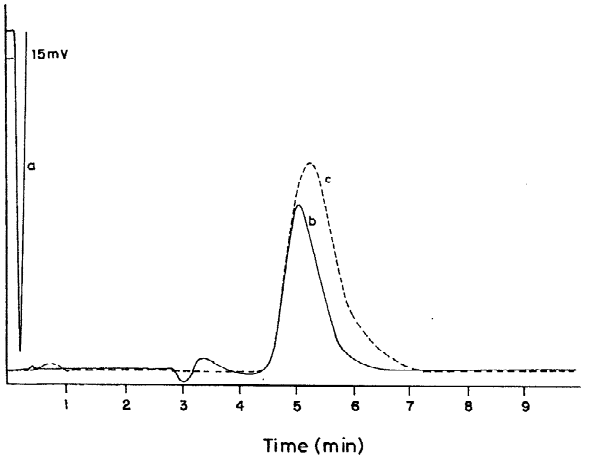

Fig. 5. Chromatograms of a waste water (sample no. 1, pink) sample. (a) Run without dialysis showing the original level of interference from dyes (shown in the same scale as b and c). (b) Revealing the peak of Cr(VI), run by dialyzed (optimized method) injection. (c) Showing the increased peak of Cr(VI), run similar to (b) but with a Cr(VI) spike of 100 μg/l.

with the help of a calibration graph. The calibration was done with standard (certified reference) solutions of Cr(VI) prepared using phosphate buffer of pH 8.0 by following the on-line dialysis IC procedure. The results are provided in Table 3. The peaks were with good shape and reproducible retention times and the chromatograms of the wastewater sample (sample no. 1, pink) obtained with and without dialyses are shown in Fig. 5(a,b). The sample was also spiked with Cr(VI) and recovery is reported in Table 3; the chromatogram for the same is shown in Fig. 5(c). Results for wet solid waste (sample no. 2, reddish brown) with and without dialyses along with recovery studies done by spiking are provided in Table 3 and the chromatograms are shown in Fig. 6-I (a,b) and 6-II (b,c). Adopting this technique, several hundreds of samples have been analyzed in the past 26 months and the results of samples of different colours and of Cr(VI) concentrations from a complete absence to different levels are presented in Table 3.

To cross-check the method developed for the quantification of Cr(VI), an alternate method like photometric technique was chosen. A wastewater sample was chosen which was free from any colour

Table 3
Cr(VI) values obtained for real samples (From five experiments)

Sample no.	Type of sample (colour of sample)	Actual amount of Cr(VI) (μg/l)	Spiked amount of Cr(VI) (μg/l)	Total conc. of Cr(VI) found (μg/l)	% Recovery	%RSD
1	Wastewater (pink)	140	100.0	237.0	97.0	0.7
2	Wet-solid waste (reddish brown)	26.5	100.0	131.6	105.1	1.0
3	Waste water (red)	3.5	50.0	53.0	99.0	1.4
4	Wastewater (wine red)	Not detected	20.0	20.4	102.0	1.2
5	Wastewater (black)	95.7	100.0	196.1	100.2	0.9
6	Waste water (blue)	Not detected	20.0	21.0	105.0	1.9
7	Waste water (indigo)	Not detected	20.0	19.8	99.0	1.7
8	Waste water (orange)	Not detected	20.0	19.7	98.5	1.2
9	Wet solid waste (pink)	Not detected	20.0	19.2	96.0	1.6
10	Wet solid waste (yellow)	2012.0	50.0	2060.4	99.9	1.4

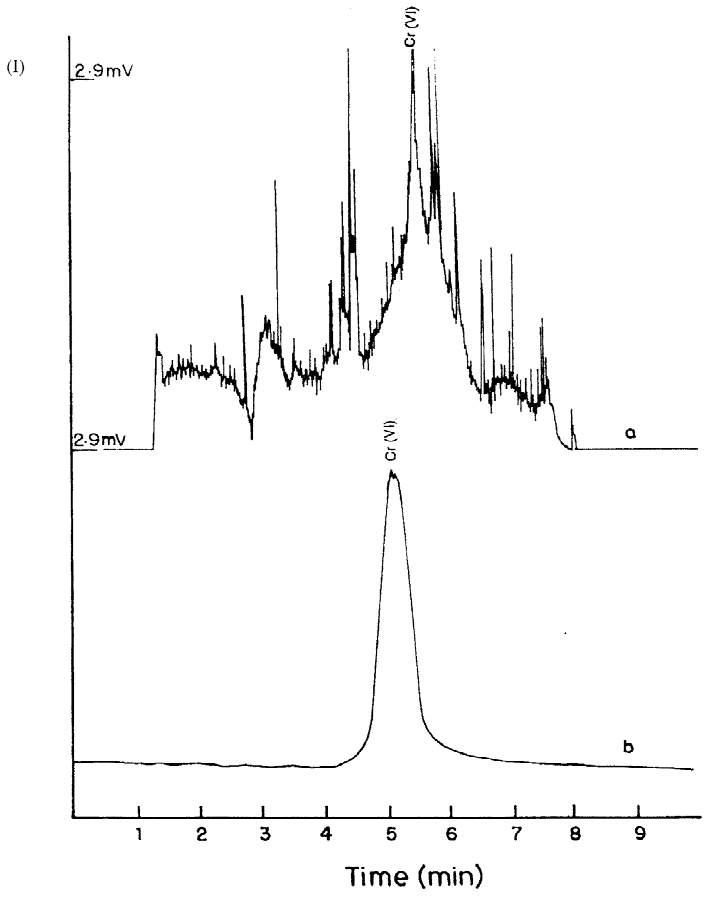

Fig. 6. (I) (a) Chromatogram of the extract of wet solid waste (sample no. 2, reddish brown) run without dialysis showing the level of noise distorting the Cr(VI) peak. (b) Chromatogram of the same run by dialyzed (optimized method) injection. (II) (b) The same chromatogram as (I) of wet solid waste. (c) The same with Cr(VI) spiked at 100 μg/l. Both were produced by dialyzed injection (optimized method).

but containing 1460 μg/l of Cr(VI) as determined by photometry. The photometric method involved all the sample preparation steps as described in Section 2.3.1, followed by Cr(VI) derivatization with 1,5-diphenylcarbazide in acidic conditions and with detection at 540 nm. The same sample when subjected to the on-line dialysis IC method discussed above, gave a value of 1474 μg/l of Cr(VI). This supports the validity of dialysis sampling method for Cr(VI) quantification. The linear dynamic range of the method is 5 μg/l to 10 mg/l. The precision was found satisfactory with %RSD not exceeding 2.0 from five replicates and a detection range of 5–10 000 μg/l.

4. Conclusions

On-line dialysis for IC technique serves well to eliminate water-soluble anionic dyes as evidenced from the direct injection and dialysis studies of environmental samples containing various dyes. The recovery studied from Cr(VI) spiked samples assures a high confidence level for this technique. The method has detectability down to 5 μg/l, estimated as the concentration of the analyte which gave a signal that was three times above the mean blank signal. The method is excellent for trace level detection of Cr(VI). This methodology is suitable for a reliable analysis of Cr(VI) in various environmen-

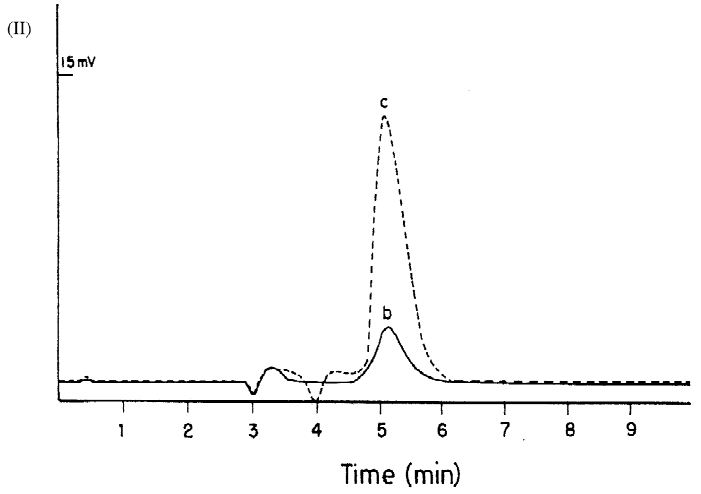

Fig. 6. (*continued*)

tal samples, dyes and other coloured matrices. The technique can be extended to trace level detection of other inorganic ions in organic matrices constituting dissolved and particulate matter.

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