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Sensitive determination of chromium (VI) in paint samples using a membrane optode coupled to a multisyringe flow injection system

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ABSTRACT

In this work, the potential of a membrane optode coupled to a multisyringe flow injection system (MSFIA) was assessed for determining the Cr(VI) concentration in paint samples. The detection is based on the color obtained from the reaction of Cr(VI) with 1,5-diphenylcarbazide in the presence of sulfuric acid (H_2SO_4). The redox product was immobilized on a poly(styrene-divinylbenzene) (SDB-XC) membrane optode. The analyte in the sample was then directly quantified at the surface of the disk by measuring the intensity of reflected incident light using a bifurcated optical fiber at 540 nm. Experimental parameters (concentration of reagents, sample volume, flow rate of sample solutions, eluent concentration, and effect of diverse ions) were studied in detail. The overall time required for the complete procedure was 4 min and only required 0.2 mL of the sample volume. The dynamic working response of Cr(VI) was found within the concentration range of 2.4–1000 $\mu g\,L^{-1}$ with a limit of detection (LOD) of 0.7 $\mu g\,L^{-1}$, while the relative standard deviation (RSD) for 400 $\mu g\,L^{-1}$ Cr(VI) was lower than 2% ($n=6$).

This developed method was used to determine Cr(VI) concentrations in the paint samples, for which an alkaline extraction procedure was proposed. The extraction procedure was based on the use of a 7.5% Na_2CO_3/5% NaOH solution at 90 °C for 30 min. Under optimal conditions, the recoveries ranged from 99% to 101%. The complete method was validated using a certified reference material (ERA-QC540, soil sample) and by comparing the results with those obtained using atomic absorption spectrometry (AAS).

1. Introduction

There is currently increasing interest in determining trace amounts of hazardous substances, such as heavy metals, because of the persistent and bioaccumulative effect they have on the environment and living organisms. Hexavalent chromium [Cr(VI)] is extremely toxic and exhibits mutagenic and potential carcinogenic effects [1–3]. A common source of Cr(VI) exposure is through Cr(VI) based paint. Chromate-based pigments, such as strontium chromate, zinc chromate, calcium chromate and lead chromate, are commonly used in anti-corrosive primers and top coat paints because of their durability and corrosion resistance. Additionally, various Cr(VI) paints are used during the production of toys and in painting materials for children. There are serious concerns about the use of chromium in these materials because of the known ability of heavy metals to leach out of children's toys and through contact with materials used for drawing. Some of the developed countries have established limits on the Cr(VI) content in paints. For example, the European Community (EC) has implemented legislation regarding the Cr(VI) content in paints used for toys and other articles for children (88/378/EEC-2009, EC); this regulation recommends a limit of 0.02 mg Cr(VI) kg^{-1} [4].

For these reasons, the development of analytical methodologies capable of determining trace levels of Cr(VI) in paint samples has been arousing interest, mainly due to their prominence, in terms of quality control and environmental factors.

The analysis of Cr(VI) in paint samples requires two major steps: extraction and quantitative determination. An optimal extraction procedure should completely extract the Cr(VI) species without interconverting between the different chromium oxidation states during sample preparation [5,6]. In this sense, several methodologies have been proposed involving alkaline buffers for extracting and dissolving Cr(VI) species from environmental samples [6]. The most prevalent method used for determining the Cr(VI) concentration in soils, sediments, and sludges is the revised method 3060A of the United States Environmental Protection Agency (EPA) [7]. In this method, the sample is extracted using a 2% Na_2CO_3/3% NaOH solution for 60 min. Method 7604 of the National Institute for Occupational Safety and Health (NIOSH) describes the use of a 2% NaOH/3% Na_2CO_3 extraction solution for up to 90 min for determining the concentration of insoluble chromates in paint aerosol [8]. Method ID-215 of the Occupational

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Safety and Health Administration (OSHA) utilizes a two-step extraction procedure for determining the concentration of Cr(VI) in air samples from spray-painting work places first using a 10% Na_2CO_3/2% $NaHCO_3$ solution for 60–90 min. The extraction yield of this method is improved using a second step that involves the use of a hot 5% NaOH/7.5% Na_2CO_3 solution for an extra few minutes [9]. Sabty-Daily et al. [10] reported a two-step alkaline digestion using NIOSH method 7604 and 1,4-dioxane for extracting Cr(VI) from paint samples. Currently, there is a consensus on the use of an alkaline extraction solution containing a variable concentration of NaOH/Na_2CO_3 with the addition of $MgCl_2$ and phosphate at temperatures of 90–95 °C to achieve minimal interconversion between species and maximum extraction efficiency of hexavalent chromium from solid materials; however, there is variability in the extraction time in these reports [11].

There are several analytical techniques that have been used to determine the chromium concentration including inductively coupled plasma atomic mass spectrometry (ICP-MS) [12,13], atomic emission spectrometry (ICP-AES) [14–16] and atomic absorption spectrometry (AAS) [17–20]. However, most of these methods have the disadvantage of using high cost instruments and require a preconcentration step to enrich the analyte or to eliminate matrix effects.

With regard to the isolation and subsequent enrichment of the target species, this is accomplished using solid-phase extraction procedures that have been consolidated as valuable sample pretreatment strategies [21]. Direct optosensing at the solid surface avoids the disadvantage of traditional sorbent extraction methods that involve extracting the analyte onto a proper support loaded with a colorimetric reagent, which can then be quantified directly on the adsorbed surface using reflectance spectroscopy [21,22]. The most prevalent colorimetric method for determining the Cr(VI) concentration uses a selective reaction with 1,5-diphenylcarbazide (1,5-DPC) in a sulfuric acid medium, which results in the formation of a red-violet Cr(III)-1,5-diphenylcarbazone complex [23,24]. The direct analysis of the analyte on the surface of the adsorbent matrix is convenient because of its simplicity and rapidity for routine analysis.

Recent advances in the automation of flow systems include the development of the multisyringe flow injection analysis (MSFIA) technique, which has gained great interest in recent years [25]. It was reported that this flow injection system, when compared to their off-line batch methods, offers a number of significant advantages for ultra-trace determinations: greater efficiency, lower consumption of sample and reagents, improved precision, reduced risk of contamination and increased sampling frequency [26]. To date, flow-based membrane optode procedures coupled to MSFIA have been developed to determine the concentrations of environmental pollutants such as 1-naphthylamine [27], nitrates [28], sulfide [29] and nitrophenol derivatives [30].

In this work, a membrane optode coupled to MSFIA using a poly (styrene-divinylbenzene) membrane disk (SDB-XC) as a solid phase for determining the Cr(VI) concentration in paint samples was described. 1,5-diphenylcarbazide was used as the derivative agent. Detection was performed by measuring the intensity of the reflected incident light at the surface of the disk using a bifurcated optical fiber at 540 nm. The analysis of Cr(VI) in the paint required a key sample preparation step, which was also one of the purposes of this research.

2. Materials and methods

2.1. Reagents

All of the chemicals were analytical reagent grade. Millipore purified water (18 MΩ cm, Millipore, Billerica, MA, USA) was used throughout the study. A stock standard solution of 1000 mg L^{-1} of chromium (VI) was acquired from the Ricca Chemical Company (Arlington, TX, USA). Working solutions were prepared by the proper dilution of the stock solution with purified water. The color chelating agent was prepared by dissolving 0.15 g of 1,5-diphenylcarbazide (Alfa Aesar, Ward Hill, MA, USA) in a 50 mL volumetric flask and then diluting with acetone, which was stored in a Teflon bottle in a freezer. A 0.1 mol L^{-1} H_2SO_4 solution was prepared from concentrated sulfuric acid (Sigma-Aldrich, Steinheim, Germany). Sodium hydroxide, magnesium chloride, and anhydrous sodium carbonate were obtained from Sigma-Aldrich (Steinheim, Germany). Methanol and acetone were HPLC grade (Fermont, Monterrey, Mexico). Hydrochloric acid and nitric acid were obtained from Tedia (Trace Metal Grade, Fairfield, OH, USA).

The 0.5 mm thick poly (styrene divinylbenzene) copolymer (SDB-XC) disk, which was kindly provided by 3M Empore (St. Paul, MN, USA), was cut into small membrane disks with a diameter of 8 mm for the optode flow-cell.

The method was validated using the certified reference material ERA QC 540 (metals in soil, Era Waters Inc. CO, USA).

2.2. Instrumentation

The membrane optode coupled to the MSFIA system for determining the Cr(VI) concentration is schematically illustrated in Fig. 1. The manifold consists of one multisyringe module (BU-4-S, Crison, Alella, Barcelona) equipped with four 5 mL syringes S1–S4 (Hamilton Bonaduz AG, Switzerland). Each syringe had a three-way solenoid valve (N-Research, Caldway, NJ, USA) at the head (V1–V4), which facilitates the application of multicommuted schemes. The multisyringe module also contained two external solenoid valves (V5 and V6) that were crucial for the performance of the protocol.

The optode flow-cell (SCIWARE, Palma de Mallorca, Spain) (see inset in Fig. 1) was comprised of two opaque square blocks made of poly (ether ether ketone) (PEEK). The block also had a thin plastic window that covered the face of the optical fiber to protect it from aggressive reagents. A 0.5 mm thick PTFE spacer with a 1 × 0.1 slot, which determines the flow path and the effective retention zone, was placed between the two blocks. The membrane disk was located on a polyethylene frit (12 μm pore size) held on a PVC fitting, which constituted the disk holder.

The manifold was built using 0.8 and 1.5 mm i.d. polytetrafluoroethylene (PTFE, Teflon). The miniaturized optical detector consisted of a diode array USB2000 spectrophotometer (Ocean Optics, Dunedin, FL, USA) and a Light-Emitting Diode (LED), which illuminates at high intensity when an electrical current is passedthrough it (0.42 mA). The LED emission spectrum was from 400 to 800 nm in the visible region. The LED was connected to an adjustable power supply. The light source was attached to the optode flow-cell (see Fig. 1) via one arm of the bifurcated optical fiber (R400-7-UV/VIS, Ocean Optics) with an internal diameter (i.d.) of 400 μm. The reflected radiation was returned to the detector through the other arm of the optical fiber. The analytical wavelength used for monitoring Cr(VI) was 540 nm. Instrumental control, data acquisition and data processing were performed using the software package Autoanalysis 5.0 (SCIWARE, Palma de Mallorca, Spain).

The determination of the total chromium content in the samples was performed using a GBC model 932 AA atomic absorption spectrometer (GBC Co., Victoria, Australia), which was equipped with a chromium hollow cathode lamp using an air–acetylene flame.

2.3. Procedure

Membrane optode-MSFIA procedure. The valves in the Off position (Fig. 1) were connected to the right channel, and the valves in the On position were connected to the left channel. The

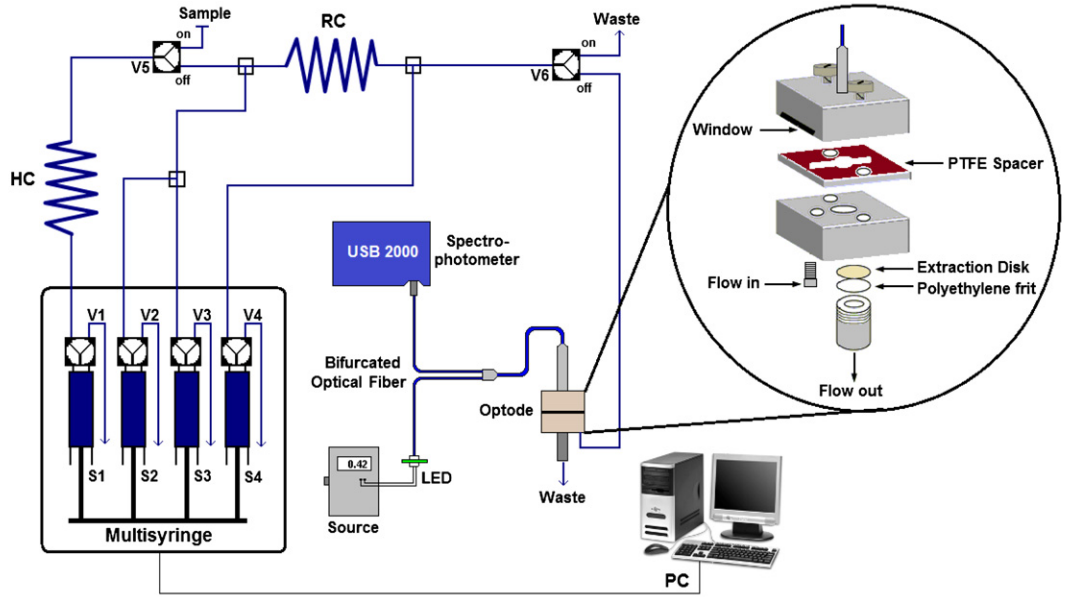

Fig. 1. Schematic representation of the MSFIA membrane optode manifold designed for the determination of Cr(VI) in paint samples using 1,5-diphenylcarbazide (1,5-DPC) as derivatizing agent. HC: Holding coil; RC: Reactor coil. Syringes content: S1 water, S2 1,5-DPC , S3 H_2SO_4, and S4 eluent (methanol/HCl).

Table 1
Protocol sequence programed for the determination of Cr(VI) by membrane optode coupled to MSFIA system.

Step	Volume (mL)	Flow rate ($mL\ min^{-1}$)	Position of solenoids valves						Description
			V1	V2	V3	V4	V5	V6	
1	5.0	10.0	Off	Off	Off	Off	Off	Off	Loading reagents (S2–S4 and V2–V4) into syringes
2	0.2	15.0	On	Off	Off	Off	On	Off	Loading sample (S1,V1,V5) into HC
3	0.2	0.5	Off	Off	On	Off	Off	On	Dispensing H_2SO_4 (S3,V3,V6) into RC
4	0.1	1.0	Off	On	Off	Off	Off	On	Dispensing 1,5-DPC (S2,V2,V6) into RC
5	0.2	0.3	On	Off	Off	Off	Off	On	Dispensing sample (S1,V1,V5, V6) into RC
6	1.5	10	On	Off	Off	Off	Off	On	Formation of complex (S1,V1,V5, V6) into RC
7	3.0	1.5	On	Off	Off	Off	Off	Off	Preconcentration and detection (S1, V1, V5, V6) into membrane optode
8	1.0	1.5	Off	Off	Off	On	Off	Off	Dispensing eluent (S4,V4,V6) to regenerate the membrane optode
9	–	–	Off	Off	Off	Off	Off	Off	Stop measurement and turn off solenoids valves
10	–	–	Off	Off	Off	Off	Off	Off	The system is once again ready to begin the process

syringes S1, S2, S3 and S4 with their commutation valves (V1, V2, V3 and V4) contained the sample, 3 $mg\ mL^{-1}$ of 1,5-diphenylcarbazide (1,5-DPC), 0.1 $mol\ L^{-1}$ sulfuric acid and the eluent (methanol/0.3 $mol\ L^{-1}$ HCl, 90:10), respectively. Furthermore, two additional three-way solenoid valves (V5 and V6) were coupled to the system for injecting the sample and deviating the flow for cleaning procedures, respectively. Table 1 shows the programmed protocol sequence used for determining the Cr(VI) concentration using the membrane optode coupled to the MSFIA system.

For this reaction, syringe S3 and valves V3, V6 dispensed the sulfuric acid into the reaction coil (RC, valve V6 in the On position); syringe S2, and valves V2, V6 dispensed the 1,5-DPC into the RC; and syringe S1 and valves V1, V5 dispensed the samples toward the RC that was previously loaded into the holding coil (HC) (valve V5 in the Off position and V6 in the On position). The redox reaction between Cr(VI) and 1,5-DPC in acidic medium and the formation of the red–purple complex with a maximum absorption signal at 540 nm were achieved in the RC. Syringe S1, valves V1, V5 and V6 (On, Off and Off positions, respectively) injected the carrier (water) to transfer this complex to the membrane optode where the *in situ* preconcentration/detection was performed on an SDB-XC extraction disk. After the complex was preconcentrated and detected, it was eluted by syringe S4 and valves V4, V6 (On and Off positions, respectively) using the methanol/HCl mixture. Therefore, the sorbent material was rendered ready for beginning a new operational cycle. For experiments related to the determination of chemical and physical parameters, the membrane was changed once a day. For analysis of real samples, the membrane was replaced whenever baseline drift was noticed, typically after 30–40 analyses.

Alkaline extraction procedure. Commercial yellow acrylic paint samples and a chromate-based pigment obtained from a local market were extracted using the proposed extraction procedure and analyzed for hexavalent chromium using the developed MSFIA system and AAS, for comparative purpose. Briefly, 1 g of sample was weighed into a 15 mL tube followed by the addition of 5 mL of a 5% NaOH/7.5% Na_2CO_3 solution. Then, 40 mg of $MgCl_2$ and 50 μL of 1 $mol\ L^{-1}$ K_2HPO_4/KH_2PO_4 buffer (pH 7) were added, and the sample solutions were heated to 90–95 °C during 30 min. The samples were then cooled to room temperature, centrifuged and filtered using a 0.45 μm Nylon filter. The pH of the filtered solution was adjusted to 7 using 2 $mol\ L^{-1}$ HNO_3, and then the solution was diluted to 10 mL with ultrapure water; afterwards, the sample was analyzed using the membrane optode-MSFIA system (0.2 mL) and by AAS (3 mL).

Digestion procedure. For determining the total Cr content, an acid digestion procedure based on the 3052 EPA protocol [31] was performed. Briefly, 0.5 g of sample was weighed into a 15 mL tube followed by the addition of 5 mL of HNO_3 and 1 mL of HCl. The samples were heated at 90 °C for 2 h. After cooling, the solutions were transferred into a 15 mL tube and diluted to 10 mL with ultrapure water. The samples were properly stored for subsequent AAS analysis.

3. Results and discussion

A membrane optode coupled to a MSFIA system was evaluated for determining trace levels of Cr(VI) in paint samples. The measurements were expressed as a function of reflectance ($F(R)$). The Kubelka–Munk function has been proposed for the analysis of diffuse reflectance from opaque and thin layers [27] and relates the analyte concentration (C) to the reflected light intensity as follows:

$$F(R)=\frac{(1-R)^2}{2R}=\varepsilon CS$$

where R represents the ratio of the net sample signal reflected radiation intensity in the presence of the analyte (sample signal minus blank signal) to that without analyte, ε is the molar absorptivity and S is related to the scattering. Reflectance measurements were performed at 540 nm, which is where the maximum of the reflectance spectrum was observed. The formation of the colored complexes involved two steps: (1) reduction of Cr(VI) to Cr(III) and the oxidation of 1,5-DPC to 1,5-diphenylcarbazone (1,5-DPCN); (2) subsequent formation of the color complex of Cr(III) and 1,5-DPCN [23,24,32]. The precise structure of this complex is not known, but it appears to be a cationic complex [Cr(III)-1,5-DPCN]$(^{3-n})^{+}$ [33].

3.1. Selection of chemical and flow injection parameters

The selection of the major chemical parameters of the proposed membrane optode-MSFIA system was accomplished for a Cr(VI) concentration of 1000 µg L^{-1}. This selection was focused on minimizing the consumption of reagents without sacrificing other relevant analytical features of the system. The optimization of the parameters was performed using the univariant method.

The variation of the reflectance resulting from the reaction of the 1000 µg L^{-1} Cr(VI) standard solution with 1,5-DPC in concentrations ranging from 3 to 7 mg mL^{-1} was recorded. In the investigated range of concentrations, practically no effects on the signal response were observed (Fig. 2a); therefore, the concentration of 3 mg $mL^{-1}$of 1,5-DPC was selected.

The reaction between Cr(VI) and 1,5-DPC is highly dependent on the pH [7,32]. The conventional procedure uses H_2SO_4 at a concentration of 0.1 mol L^{-1} (pH ~ 1) as the medium for the full color development of the Cr(III)-1,5-DPCN complex. According to the literature, for concentrations of acid less than 0.05 mol L^{-1}, the color does not immediately develop, and the complex is less stable when the concentrations of acid are greater than 0.1 mol L^{-1} [34,35]. As observed in Fig. 2b, the highest sensitivity was achieved with a 0.1 mol L^{-1} H_2SO_4 solution. Therefore, the selected concentrations were 3 mg mL^{-1} 1,5-DPC and 0.1 mol L^{-1} H_2SO_4.

Once the chemical variables were set at the stated values, the influence of the MSFIA parameters was studied by injecting a 1000 µg L^{-1} Cr(VI) solution with different volumes of sample, 1,5-DPC and H_2SO_4. The length of the tubing from the RC to the membrane-optode was the minimum possible distance (20 cm) to minimize dispersion. The effect of sample volume on the signal intensity was studied from 50 to 400 µL. The result is shown in Fig. 3a. The maximum reflectance intensity increased with an increase in sample volume from 50 to 200 µL, but a further increase to 200 µL resulted in a decrease in the reflectance peak intensity. A sample volume of 200 µL was chosen for further studies. The studies examining the effects of the 1,5-DPC volume between 50 and 400 µL revealed that the analytical signals increased with volumes up to 100 µL. Larger 1,5-DPC volumes resulted in a significant decay in sensitivity; therefore, subsequent studies were performed using 100 µL of 1,5-DPC (see Fig. 3b). With regard to the H_2SO_4, a volume of 200 µL resulted in the best conditions in terms of sensitivity (Fig. 3c).

The flow rate of the different steps in the experimental schedule listed in Table 1 was evaluated. The flow rate and configuration of the RC were selected by only taking into account the requirements of the reaction. The effects of the flow rates of the H_2SO_4 and 1,5-DPC solutions were investigated using the determination of the Cr(VI) standard (1000 µg L^{-1}). As observed in Fig. 4, the signal intensities were monitored using flow rates of 0.25–3.0 mL min^{-1} for all solution streams. For H_2SO_4, the highest sensitivity was obtained at lower flow rates. A flow rate of 0.5 mL min^{-1} was chosen because it provided a good signal and repeatability. For 1,5-DPC, the peak signal intensity increased with the 1,5-DPC solution flow rate up to 1 mL min^{-1}; the signal intensity decreased considerably at flow rates greater than 1.7 mL min^{-1}. Therefore, the optimal flow rates were selected to be 0.5 mL min^{-1} for H_2SO_4 and 1.0 mL min^{-1} of 1,5-DPC solution. A knotted RC was selected in an

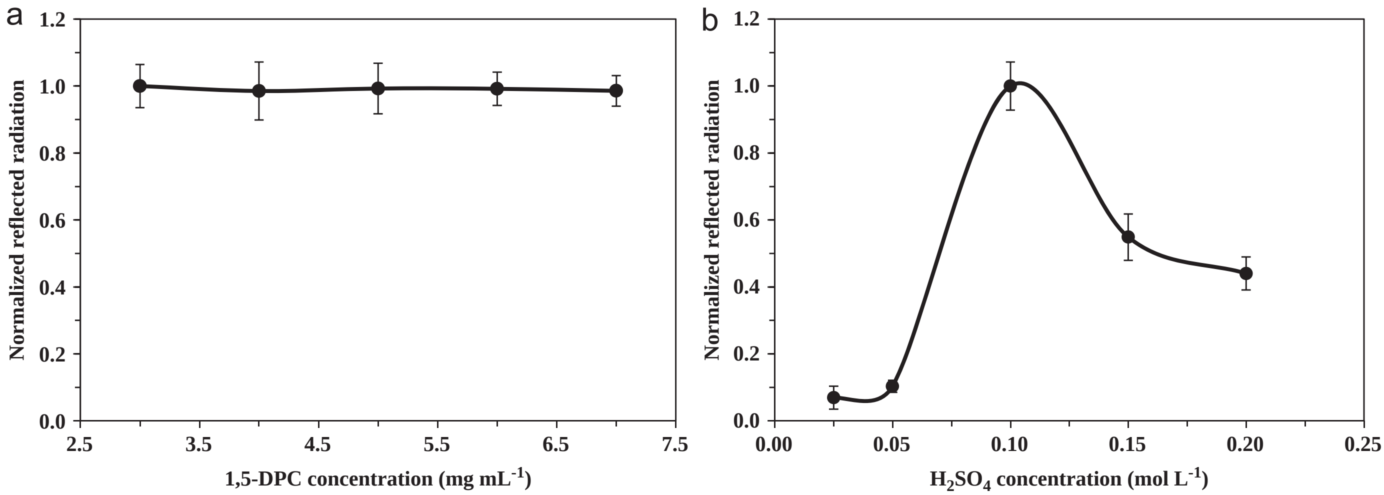

Fig. 2. Effect of (a) 1,5-DPC and (b) H_2SO_4 concentrations on the mean normalized reflected radiation (n=4) of 1000 µg L^{-1} Cr(VI) standard solution.

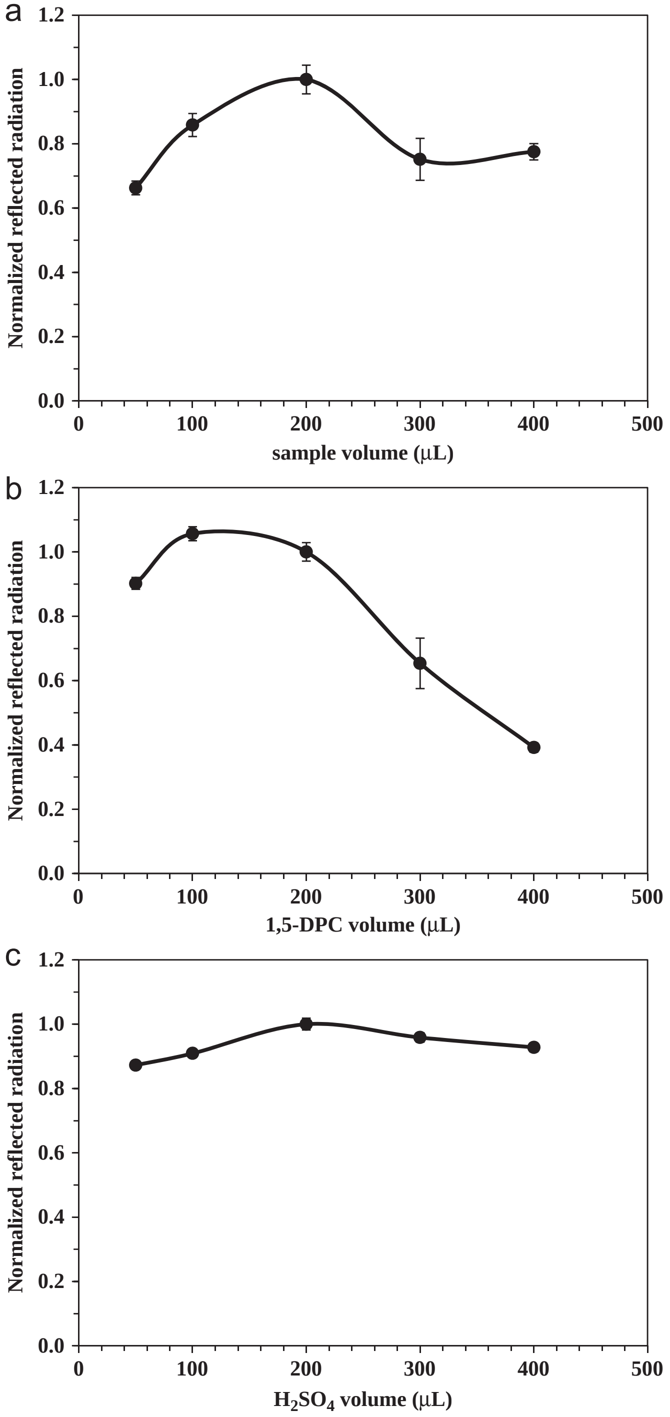

Fig. 3. Effect of (a) sample, (b) 1,5-DPC and (b) H_2SO_4 volumes on the mean normalized reflected radiation (n=4) of 1000 μg L^{-1} Cr(VI) standard solution.

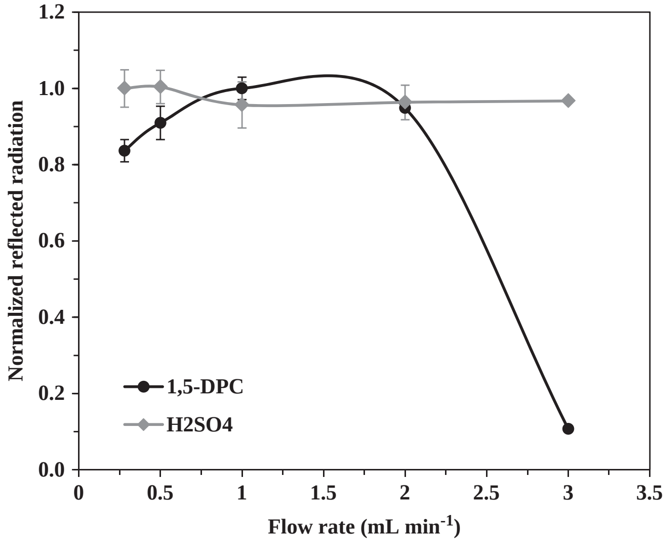

Fig. 4. Effect of 1,5-DPC and H_2SO_4 flow rates on the mean normalized reflected radiation (n=4) of 1000 μg L^{-1} Cr(VI) standard solution.

attempt to achieve a lower axial dispersion, a better reagent/sample radial mixing and to guarantee high reaction yields [29]. Systematic experiments showed that the signal intensity due to the reaction between the Cr(VI) and 1,5-DPC reagent in H_2SO_4 was not significantly influenced by the order of addition of the reagents. To allow the redox reaction of 1,5-DPC and Cr(VI) in acidic media [23,24,32], the reagents were mixed in the reaction coil in the following order: H_2SO_4 followed by 1,5-DPC and sample using a sandwich-type mixing model [36]. By using this order, the diffusion of the reagents was improved facilitating the redox reaction. The mixing flow rate of the reagents after passing through the RC was as high as possible (10 mL min^{-1}) to ensure an effective reaction mixture and repeatability.

The effect of the loading flow rate on the analytical response was studied in the range of 0.5–2.0 mL min^{-1}. The sensitivity increased up to 1.5 mL min^{-1}, and it remained constant at higher flow rates. As a compromise between sensitivity and sampling frequency, a flow rate of 1.5 mL min^{-1} was selected. Loading flow rates ≤ 2 mL min^{-1} are typically recommended for optosensing approaches whenever sorption/elution processes are involved [28]. The elution flow rate was fixed at 1.5 mL min^{-1} because the elution rate is not a critical parameter during solid-phase optosensing as the analytical signal is recorded during the retention process.

The elution of Cr(VI) from polystyrene divinylbenzene (SDB-XC) membranes was examined using solutions containing percentages of methanol in 0.3 mol L^{-1} HCl ranging from 50 to 100% (v/v). It was found that a 90% methanolic solution in 0.3 mol L^{-1} HCl was the most suitable eluent for this purpose. This solution also permitted a short membrane regeneration time, which is defined as the time required for the sensor to reach the base line signal after the maximum reflectance is reached.

3.2. Effects of diverse ions

The effects of potential interferences occurring in paint samples on the on-line MSFIA-optode determination of Cr(VI) were tested for 400 μg L^{-1} of Cr(VI) using the optimized experimental conditions. A species was considered as an interfering species if it causes a variation of more than ±5% in the analytical signal when compared to the analytical signal obtained in the absence of the interfering species.

The selectivity was evaluated for several cations and anions that are normally present in paint samples. It is well known that Fe^{3+}, Cu^{2+}, and Mo^{6+} react with 1,5-DPC, and hence, can interfere in the determination of Cr(VI) [7–9,32]. Na^{+} and Ba^{2+} could be tolerated up to at least 1000 mg L^{-1}; Cu^{2+} at 300 mg L^{-1}, Mo^{6+} at 5 mg L^{-1}, and Zn^{2+} and Pb^{2+} at 2 mg L^{-1}; in the case of Fe^{3+}, it was tolerated at 300 mg $L^{-1}$when it was masked with 5 mol L^{-1} ammonium hydroxide. Common inorganic anions, such as CO_3^{2-}, Cl^{-}, and PO_4^{3-}, did not interfere in the determination of

Cr(VI) and were tolerated up to at least 1000 mg L^{-1}, and $SO_4^{2-}$was tolerated at 700 mg L^{-1}.

3.3. *Analytical performance of the proposed system*

The figures of merit corresponding to the proposed system are summarized in Table 2. The linear dynamic range was from 2.4 to 1000 μg L^{-1} with a correlation coefficient (r) of 0.9996. The limit of detection (LOD) was calculated as $3S_b/S$, where S_b is the standard deviation for 10 measurements of the blank and S is the slope of the calibration graph. The repeatability and reproducibility of the MSFIA-optosensing system were checked using nine replicate measurements of 400 μg L^{-1} Cr(VI). An injection throughput of fifteen injections per hour for a sampling volume of 0.2 mL was achieved.

3.4. *Influence of the critical parameters on the extraction procedure*

The developed membrane-optode system was used to determine Cr(VI) in the paint samples. The Cr(VI) from the paint samples was extracted using an alkaline extraction procedure. A 2^2 factorial design was used to ascertain which factors have significant influence on Cr(VI) extraction from paint samples. The investigated factors and their respective levels are given in Table 3. These experiments were performed in triplicate and in random order. The levels were selected on basis a preliminary studies [7–9], since mild extraction conditions have been recommended to avoid chromium species intercoversion for the analysis of soil and sediments [6]. The extraction procedure was evaluated using white paint (no chromate-based paint) spiked with 8 mg Cr(VI)/kg. The variables evaluated during the extraction were the time and the composition of the extracting agent. The percent recovery was used as the analytical response. Numerical analysis of the data resulting from the experimental design was performed using the statistical package STATISTICA 6.1, StatSoft, Inc. (2002), USA. This fit model presented an adjusted square correlation coefficient (R^2 adjusted) of 95.12%, which was very well fitting with the statistical model.

Table 2
Analytical features of the MSFIA-optosensing system for Cr(VI) determination using disk-based solid phase preconcentration.

Analytical parameter	Value
Lineal regression equation	$F(R)=2.9311[\text{Cr(VI)}]\mu g\ L^{-1}+62.413$
Correlation coefficient (r)	0.9996
Lineal dynamic range	2.4–1000 μg L^{-1}
LOD	0.7 μg L^{-1}
LOQ	2.4 μg L^{-1}
Repeatability (25 μg L^{-1})	3.5
Repeatability (400 μg L^{-1})	1.9
Reproducibility (25 μg L^{-1})	6.2
Reproducibility (400 μg L^{-1})	4.3
Injection frequency	15 samples h^{-1}

From the results reported in Table 3, a Pareto chart (Fig. 5) was plotted to examine the influence of the factors and their interactions in the system. An effect was considered to be significant when it was above the standard error at the 95% confidence level ($P > 0.05$), which is denoted by the vertical line on the graph. The Pareto chart showed that within the range studied, the extraction time was not a significant parameter, and it was thus kept at 30 min. The replicates did not affect the extraction procedure indicating the good reproducibility of the method. The curvature was not significant showing that a surface analysis design is not necessary for the optimization of the factors in the studied range [37]. The extracting agent and the interaction of extracting agent/time were the key factors on the extraction efficiency. While the extracting agent positively influenced the extraction efficiency; a negative effect was observed from the interaction of extracting agent/time. Thus, the proposed extraction procedure of Cr(VI) from paint samples involved the use of a NaOH (5%)/Na_2CO_3 (7.5%) solution at 90 °C for 30 min. Under this extraction conditions, a recovery percent of 99.7 ± 0.4 was achieved. Compared with the alkaline extraction procedures used for environmental samples [7–9], this procedure has the advantage of a short extraction time (30 min) without the use of organic solvents [10] that could promote interconversion between species.

3.5. *Determination of Cr(VI) content in paint samples*

The membrane optode-MSFIA system was satisfactorily applied for determining the Cr(VI) content in commercial yellow acrylic paint samples, a chromate-based pigment and a soil reference material after alkaline extraction. To check the validity

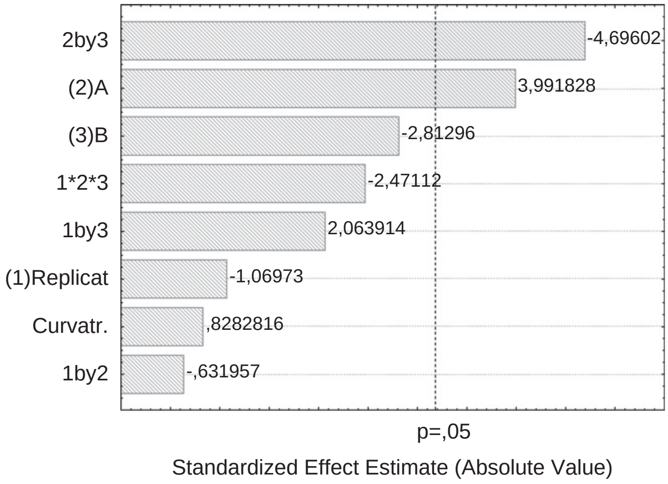

Fig. 5. Pareto chart obtained from the optimization study of the variables, with their significance, for the extraction recovery of Cr(VI) from paint samples using alkaline extraction procedure at 90 °C. (1) Replicates; (2) A: extractant agent; (3) B: time; Curvatr: curvature and their interactions factors.

Table 3
Conditions for the extraction of Cr(VI) at 90 °C and analytical response in the factorial 2^2 experimental design using detection by membrane optode-MSFIA system.

Experiment[a]	Extraction time (min)	$NaOH/Na_2CO_3$ concentration (%, w/v)	Extraction time (level)	$NaOH/Na_2CO_3$ concentration (level)	Recovery (%)[b]
1	30	NaOH (2%)/Na_2CO_3 (3%)	−	−	95.1 ± 1.8
2	30	NaOH (5%)/Na_2CO_3 (7.5%)	−	+	99.7 ± 0.4
3	90	NaOH (2%)/Na_2CO_3 (3%)	+	−	96.2 ± 1.6
4	90	NaOH (5%)/Na_2CO_3 (7.5%)	+	+	95.7 ± 1.3

[a] $n=3$ replicates per experiment.
[b] Average ± SD (SD, standard deviation).

Table 4
Determination of Cr in real samples (mean value ± 95% confidence value, $n=3$) after alkaline extraction Cr(VI) and after acid digestion (total Cr).

Sample	**Cr(VI) concentration ($mg\ kg^{-1}$)**		**Total Cr concentration ($mg\ kg^{-1}$)**
	Proposed method (optode-MSFIA)[a]	**Reference method (AAS)**[b]	
Reference material[c]	12.9 ± 0.2	12.5 ± 0.5	74.7 ± 3.1
Chromate-based pigment	279 ± 4	277 ± 1	1320 ± 280
Paint sample 1	0.71 ± 0.03	< LOD	0.76 ± 0.32
Paint sample 2	0.99 ± 0.03	1.06 ± 0.07	1.51 ± 0.13
Paint sample 3	1.03 ± 0.09	1.10 ± 0.31	1.29 ± 0.20

[a] LOD by membrane optode –MSFIA=0.018 $mg\ kg^{-1}$.
[b] LOD by AAS=0.7 $mg\ kg^{-1}$.
[c] ERA metals in soil QC540 (40–300 $mg\ kg^{-1}$ indicative value of total Cr).

of the flow-through method, the concentration of Cr(VI) in the above mentioned samples was also determined using atomic absorption spectrometry (AAS) after the alkaline extraction procedure. Table 4 compares the mean values ± 95% confidence level of the Cr(VI) concentration in real samples obtained from the proposed method and AAS. The total chromium concentration in real samples after acid digestion is also shown in Table 4. From this table, it can be seen that most of the chromium content in the paint samples was in the hexavalent form. The results showed no significant differences between the Cr(VI) concentrations obtained from the membrane optode system and AAS, except for paint sample 1 that was below the limit of detection of the flame-AAS procedure. The proposed method had a low relative standard deviation compared with AAS. Although Pb ($0.08 \pm 0.01\ mg\ kg^{-1}$) and Zn ($0.52 \pm 0.06\ mg\ kg^{-1}$) were detected in the analyzed paint samples, the developed extraction procedure seemed to have no interferences on the spectrophotometric determination of Cr(VI) using the membrane optode-MSFIA system.

4. Conclusions

A simple, highly sensitive, selective and low cost membrane optode-MSFIA system was developed for determining the Cr(VI) concentration in paint samples. The recovery rate of Cr(VI) from paint samples approached 100% when using an alkaline extraction procedure that involved the use of a 7.5% Na_2CO_3/5% NaOH solution at 90 °C in a extraction time of 30 min. The MSFIA-optosensing procedure was totally automatized and only required a low volume of sample (0.2 mL). The developed system presented good reproducibility and sample throughput, and it exhibited similar detection limits to the HG-AAS method [18] and the HPLC–ICP-MS procedure [12,13,38]. The optode system presented some advantages compared to the SPE-FIA-AAS method [17,19], such as lower detection limits and higher injection throughput. The proposed method was successfully applied to the analysis of paint samples. The results obtained using the membrane optode-MSFIA systems were comparable to those obtained from the reference method.

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