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On-line thermal lens spectrometric detection of Cr(III) and Cr(VI) after separation by ion chromatography

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Abstract

The applicability of thermal lens spectrometry for the on-line detection of trivalent and hexavalent chromium species after high-performance ion chromatographic (HPIC) separation was investigated. A collinear dual-beam thermal lens spectrometer was utilized to detect Cr species separated as anions on a Dionex HPIC CS5 column. Precolumn derivatization of Cr(III) by pyridine-2,6-dicarboxylic acid and postcolumn derivatization of Cr(VI) by diphenylcarbazide were necessary for the efficient separation and on-line detection of both Cr species. Under the proposed experimental conditions, i.e. 200-μl sample loop and an argon ion laser operating at 514.5 nm, providing 160 mW power at the sample site, detection limits of 30 and 0.3 ng/ml for Cr(III) and Cr(VI), respectively, were achieved.

1. Introduction

Some industries, such as leather tanning and chromium plating, produce wastewaters containing significant concentrations of Cr(III) and/or Cr(VI). Because of the high toxicity of dichromate species, a sensitive, precise and accurate procedure for its determination is necessary. On the other hand, Cr(III) is an essential element, and no toxic effects of Cr(III) to humans are known [1,2]. However, cytogenetic effects on fish were observed at Cr(III) concentrations below 50 ng/ml [3], which is lower than the proposed drinking water standard or threshold limit level for natural waters of the first category (100 ng/ml) [4]. Therefore, levels of Cr(III) in water must also be carefully monitored.

Cr in water can be determined by a number of standard analytical methods [5], including atomic absorption (AAS) and emission spectrometry (AES), and spectrophotometry. While graphite furnace AAS and inductively coupled plasma (ICP) AES are very sensitive and useful tools for the determination of total chromium concentration, spectrophotometry is better suited for the detection of individual Cr species. The spectrophotometric determination of Cr(VI) or Cr(III) after its oxidation and reaction with 1,5-diphenylcarbohydrazide (DPC) [6–8] is highly selective and simple. Other chromogenic reagents, such as pyridine-2,6-dicarboxylic acid (PDCA) for Cr(III), can also be applied to avoid time-consuming oxidation of Cr(III) and to permit the simultaneous measurement of Cr(III) and Cr(VI) species [8]. However, matrix effects (e.g., colour of wastewater) and some interfering ions [e.g., Fe^{3+}, V^{5+} and Hg^{2+} in the case of Cr(VI)] frequently demand prior separation of

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Cr(III) and Cr(VI) from other species. This can be achieved by different separation techniques, including high-performance ion chromatography (HPIC) [8]. In the case of HPIC, on-line spectrophotometric detection of separated chromium species is most convenient and therefore most frequently applied. However, spectrophotometry is not sensitive enough for the simultaneous and accurate on-line detection of minute amounts of Cr species, which can still be toxic {below 50 ng/ml for Cr(III) [3]}.

Spectroscopic techniques such as direct current plasma (DCP) AES, ICP-AES and ICP–MS have been reported as sensitive and selective detectors in chromatographic separations of chromium species [9–11]. Nevertheless, these techniques are not yet widely accepted for routine chromatographic analysis. Partly this can be attributed to the high cost of ICP-AES and particularly ICP–MS instruments. Relatively cheaper photothermal techniques, including thermal lens spectrometry (TLS), have been attracting attention recently. TLS is also known for its extreme sensitivity and ability to measure absorbances as low as 10^{-7} cm^{-1} [12]. Therefore, the measurement of absorbance through the thermal lens effect should, in principle provide better sensitivity and lower limits of detection (LOD) than spectrophotometry. This was also confirmed by our preliminary investigations [13], which resulted in LOD lower than 0.1 ng/ml for Cr(VI) in non-flowing systems. This LOD is comparable to or better than those obtained by coupled systems including DCP-AES and ICP-AES (5–10 ng/ml) [9,10] or ICP–MS (0.3 ng/ml) [11]. However, in contrast to ICP-AES and ICP–MS, which in principle provide better selectivity, TLS is a non-specific detection technique and therefore requires prior separation of analyte species. However, as with TLS, the selectivity of coupled ICP–AES and ICP–MS techniques when used for speciation studies also depends strongly on the separation efficiency.

TLS has already been applied for the detection of different compounds in HPLC but, to the best of our knowledge, not yet in ion chromatography. It was therefore the main objective of this work to investigate the applicability of TLS for the simultaneous on-line detection of Cr(III) and Cr(VI) species after HPIC separation.

2. Experimental

2.1. Reagents

The eluent stock solution consisted of 20 m*M* PDCA, 20 m*M* Na_2HPO_4, 10 m*M* NaI, 50 m*M* CH_3COONH_4 and 28 m*M* LiOH in 18 MΩ deionized water, Cr(III) stock solution of 1 mg/ml was prepared by dissolving 4.577 g of $Cr(NO_3)_3$ (dried at 105°C for 1 h) in 1 l of distilled water and Cr(VI) stock solution of 1 mg/ml was prepared by dissolving 2.828 g of $K_2Cr_2O_7$ in 1 l of distilled water.

2.2. Chromatographic conditions

An HPIC CG5 guard column (4 mm I.D.) and an HPIC CS5 separation column (4 mm I.D.), both from Dionex, were used. The sample volume was 200 μl. The eluent was 2 m*M* PDCA–2 m*M* $NaHPO_4$–1 m*M* NaI–5 m*M* CH_3COONH_4–2.8 m*M* LiOH in 18 MΩ deionized water at a flow-rate of 1.0 ml/min. The postcolumn reagent was 2 m*M* DPC–10% CH_3OH–0.45 *M* H_2SO_4 at a flow-rate of 0.5 ml/min.

2.3. Detection system

A dual-beam (pump–probe configuration) thermal lens spectrometer with non-focused probe beam was constructed to perform the measurements (Fig. 1). A Spectra-Physics Model 2025-05 argon ion laser or an air-cooled Omnichrome argon ion laser operating at 514.5 nm were used as an excitation source. The pump beam from the argon ion laser was modulated by a variable-speed mechanical chopper (Scientific Instruments Model 300) and focused on to the flow-through sample cell by a 100-mm focal length lens. The optimum signal-to-noise ratio was obtained at 75 Hz modulation frequency. A Uniphase helium–neon laser (Model 1103P) was used to provide the probe beam. Lens L2 was

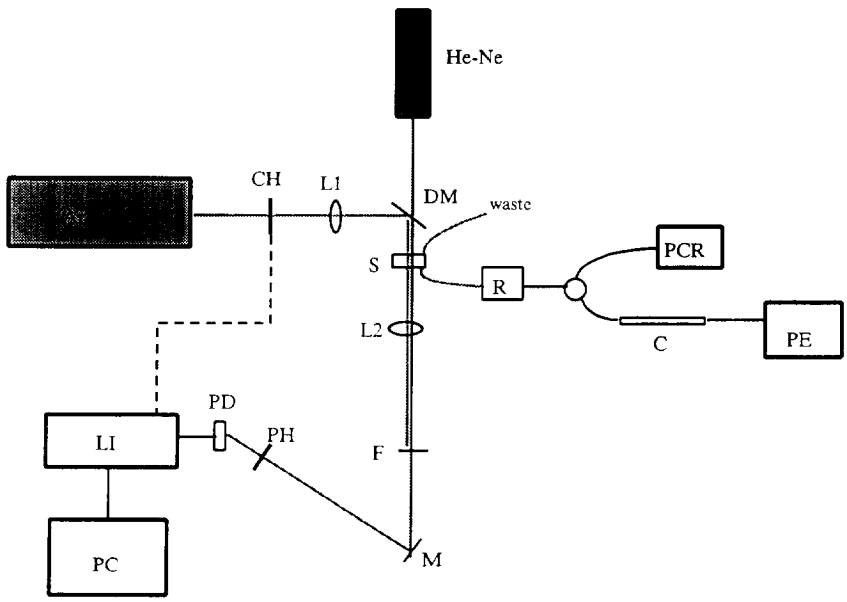

Fig. 1. Schematic diagram of the chromatographic system used in this work. PE = HPLC pump; C = column; R = postcolumn reactor; PCR = postcolumn reagent; Ar = argon ion laser; He–Ne = helium–neon laser; CH = chopper; L1 and L2 = lenses; DM = dichroic mirror; S = sample cell; F = filter; M = mirror; PH = pinhole; PD = photodiode; LI = lock-in amplifier; PC = personal computer.

used to increase the beam radius at the detector site and to facilitate sampling of the beam centre intensity. The fluctuation of the probe beam intensity was measured by a silicon photodiode (Laser Components OSD 5-E) placed 1.4 m from the sample and behind a red filter and a horizontal slit. The output of the photodiode was fed into a Stanford Research lock-in amplifier (Model SR510), which was connected to a personal computer for data processing and recording of chromatograms.

2.4. Chromatographic procedure

Cr(III) was converted into $Cr(PDCA)_2^-$ complex after adjusting the pH of the Cr(III) solution to 4 (at higher pH the precipitation of chromium oxide hydroxide occurs). Subsequently 5 ml of the Cr(III) stock solution were added to 10 ml of eluent stock solution and the mixture was heated and boiled for 1 min. After cooling, the pH was adjusted to 6.8 and the solution was diluted to 100 ml with distilled water and used as a stock solution of $Cr(PDCA)_2^-$. Samples containing known concentrations of Cr(VI) and $Cr(PDCA)_2^-$ were prepared by mixing and diluting appropriate volumes of corresponding stock solutions.

The chromatographic system depicted in Fig. 1 consisted of a Hitachi Model L-6200 HPLC pump, Rheodyne injection valve with a 200-μl sample loop, Dionex HPIC CG5 guard column and Dionex HPIC CS5 separation column attached to the on-line postcolumn reactor and further to the flow-through cell (Helma, volume 15 μl, path length 1 cm). The DPC reagent was delivered into the system at 0.5 ml/min by using a Dionex pneumatic postcolumn reagent-delivery device.

3. Results and discussion

Initial verification of the efficiency of the HPIC separation procedure [8] was performed with an air-cooled argon ion laser providing 10

mW power at the location of the flow-through cell. Retention times of about 180 and 280 s for $Cr(PDCA)_2^-$ and Cr(VI), respectively, were observed, as shown in Fig. 2. Based on a signal-to-noise ratio (S/N) of 3, the LOD was estimated to be 5 μg/ml for Cr(III) and 20 ng/ml for Cr(VI).

It is known from the theory of the thermal lens effect [12] that the relative change in the probe beam intensity ($\Delta I/I$) is proportional to the absorbance (A) and parameters such as temperature coefficient of refractive index (dn/dT), thermal conductivity (k) and probe beam wavelength (λ):

$$\frac{\Delta I}{I} = \frac{1.21A(-dn/dT)P}{\lambda k} \quad (1)$$

In addition, the thermal lens signal increases linearly with increasing laser power (P). For this reason, a more powerful laser, providing 160 mW at the location of the detection cell, was used in further experiments.

Differently from TLS measurements in non-flowing samples, the fluctuations in eluent flow strongly affect the signal stability in HPIC. Therefore, the TLS parameters such as modulation frequency and lock-in amplifier time constant must be carefully selected to maximize S/N. By selecting longer lock-in time constants, the signal was averaged over longer time intervals and the signal noise was reduced. Owing to the longer averaging periods, the chromatographic peaks were also shifted and appeared at longer retention times. These effects can be observed by comparing the chromatograms in Fig. 2 (time constant = 1 s) and Figs. 3 and 4 (time constant = 10 s).

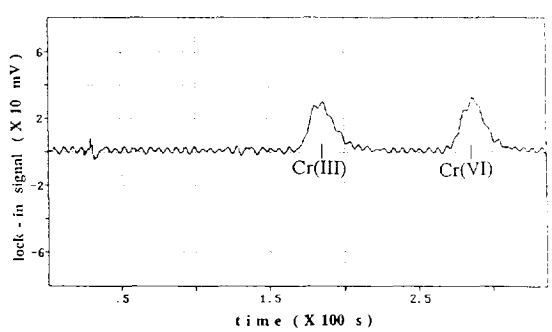

Fig. 2. Chromatogram of $Cr(PDCA)_2^-$–Cr(VI) mixture [10 μg/ml Cr(III) + 50 ng/ml Cr(VI)]. f = 8 Hz; P = 10 mW; time constant = 1 s.

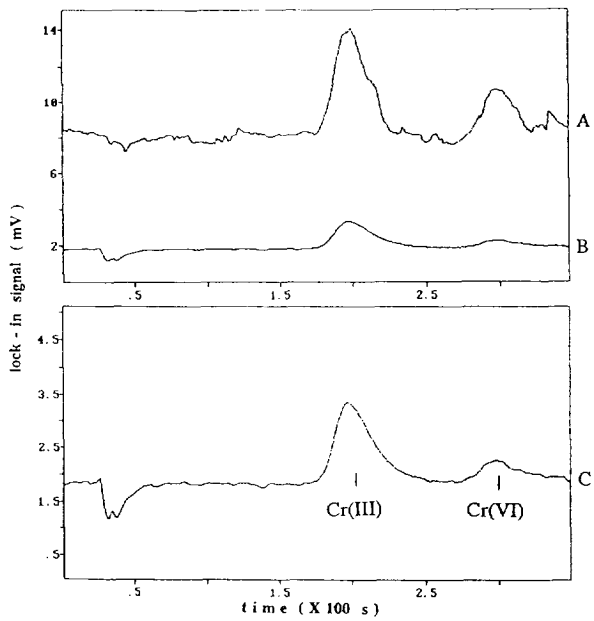

Fig. 3. Effect of chopping frequency on thermal lens signal and signal-to-noise ratio. Sample, 500 ng/ml Cr(III) + 5 ng/ml Cr(VI); P = 160 mW; time constant = 10 s; f = (A) 15, (B) 60 and (C) 60 Hz with expanded y-axis.

Additional improvements in S/N were obtained by optimizing the modulation frequency of the pump beam. A clear increase in S/N was evident when the modulation frequency was changed from 15 to 60 Hz. This is shown in Fig. 3, where a decrease of peak height can also be observed owing to the shorter excitation periods at higher modulation frequencies. However, for the same reason, the background thermal lens signal from the eluent is also reduced. Further, owing to the lock-in detection, which allows discrimination between the thermal lens signals appearing at the frequency of modulation and signals appearing at other frequencies, S/N is improved. For the experimental conditions used in this work (HPLC pump type, flow-rate), the optimum modulation frequency was found to be 75 Hz (Figs. 4 and 5).

The performance of the chromatographic sys-

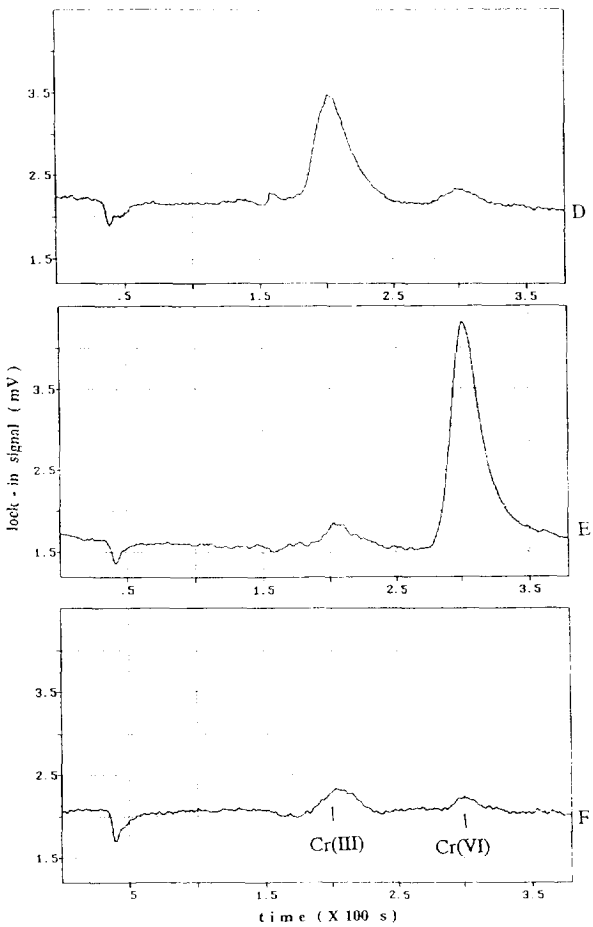

Fig. 4. Chromatograms of different $Cr(PCDA)_2^-$–Cr(VI) mixtures. $P = 160$ mW; $f = 75$ Hz; time constant = 10 s. (D) 500 ng/ml Cr(III) + 1 ng/ml Cr(VI); (E) 100 ng/ml Cr(III) + 20 ng/ml Cr(VI); (F) 100 ng/ml Cr(III) + 1 ng/ml Cr(VI).

tem with TLS detection under optimum conditions is evident from Fig. 4, which shows chromatograms obtained with samples containing different amounts of $Cr(PDCA)_2^-$ and Cr(VI). At present, the LOD ($S/N = 3$ basis), as calculated from chromatogram F (Fig. 4), is 30 and 0.3 ng/ml for Cr(III) and Cr(VI), respectively. These LODs equal the best LOD for the simultaneous determination of Cr(III) and Cr(VI) by HPIC with conventional UV–Vis detection as given in the literature [8]. It must be mentioned, however, that a detailed comparison between the results presented here and those in

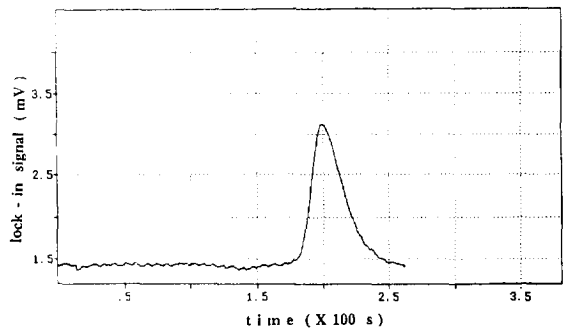

Fig. 5. Thermal lens signal in the absence of postcolumn reagent flow. Sample, 500 ng/ml Cr(III); $P = 160$ mW; $f = 75$ Hz; time constant = 10 s.

the literature is impossible, because the S/N used for the calculation of LOD is not given in Ref. [8] and the lowest concentration of Cr(VI) used to obtain a chromatogram was 3.8 ng/ml. Nevertheless, in terms of the minimum mass of Cr(III) and Cr(VI) that can still be detected, i.e., 6 ng and 60 pg, respectively, the LODs obtained by TLS are superior because of the smaller sample loop used in this work.

In addition to the use of a larger sample loop, the most significant improvement in the LOD of TLS detection in HPIC of Cr(III) and Cr(VI) is expected from stabilization of the eluent flow, which contributes to the thermal lens signal noise. To reveal the source of this signal noise, a chromatogram of Cr(III)–PDCA complex was recorded without the addition of postcolumn DPC reagent (Fig. 5). This experiment confirmed that signal instability arises primarily from periodic changes in eluent flow caused by the pulsed operation of the HPLC pump and not from the addition of DPC reagent. It is expected that better stability of the eluent flow and consequently lower baseline noise could be obtained by the use of a pulseless HPLC pump. As a result, lower LODs are expected.

The added postcolumn DPC reagent, which is needed for the detection of Cr(VI), actually dilutes the eluent and reduces the concentrations of eluted $Cr(PDCA)_2^-$ and Cr(VI) anions. The resulting decrease in peak height is clearly evident when chromatogram D in Fig. 4 is compared with the chromatogram in Fig. 5 (no DPC

added). The $Cr(PDCA)_2^-$ peak in Fig. 5 is about 30% higher, which is in good agreement with the eluent dilution factor in the case of added DPC (eluent flow-rate 1.0 ml/min, postcolumn reagent flow-rate 0.5 ml/min). This implies the possibility of obtaining an improved LOD for Cr(III) in the absence of postcolumn reagent and an improved LOD for both species by optimizing the postcolumn reagent concentration and/or flow-rate. Further improvements, which are currently under investigation, are possible by an additional increase in laser power or by application of lasers (krypton, excimer-pumped dye lasers) that better match the absorption maximum of the Cr(III) and Cr(VI) complex.

By fully exploring the potential of TLS, the LOD for the simultaneous determination of Cr(III) and Cr(VI) after HPLC separation should approach the LOD obtained for Cr(VI) in non-flowing samples, i.e., 0.1 ng/ml [13] and correspondingly 10 ng/ml for Cr(III).

4. Conclusions

It has been demonstrated that thermal lens spectrometry is a simple, rapid and sensitive method for the on-line detection of Cr(III) and Cr(VI) after HPIC separation. The LOD of 30 ng/ml for Cr(III) and 0.3 ng/ml for Cr(VI) permits the determination of Cr(III) concentrations lower than 100 ng/ml and Cr(VI) concentrations lower than 1 ng/ml in solutions containing both chromium species. Considering the smaller injection loop (200 μl), the LODs obtained are superior to those obtained with spectrophotometric detection at 520 nm [8].

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