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Effect of organic solvents in the on-line thermal lens spectrometric detection of chromium(III) and chromium(VI) after ion chromatographic separation

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Abstract

The effect of methanol, acetone and acetonitrile on the sensitivity, selectivity and the detection limits (LODs) of the determination of chromium species by ion chromatography was investigated. A collinear dual-beam thermal lens spectrometer was used for the direct detection of chromium complexes [pre-column derivatized Cr(III)–pyridine-2,6-dicarboxylic acid, and post-column derivatized Cr(VI)–1,5-diphenylcarbazide] following the ion chromatographic separation on a Dionex HPIC-CS5A solvent compatible column. Different amounts of organic solvents were added directly to the eluent (up to 30%) and to the post-column reagent (up to 60%) to improve the thermooptical properties of the solvents. Consequently, the sensitivity of the technique was increased by a factor of 2–3 and LODs of 0.1 and 10 μg dm^{-3} were achieved for Cr(VI) and Cr(III), respectively, when the eluent reaching the detector contained 30% of acetonitrile. The addition of organic solvents also resulted in significant changes in retention times, which improved the Cr(III)/Cr(VI) separation.

Keywords: Chromium; Metal cations; Thermal lens spectrometry; Detection, LC

1. Introduction

In recent years there has been growing concern about environmental pollution and speciation of trace metals has received particular attention. Metal speciation refers to the identification and quantification of chelated, organometallic or free metal ions or their oxidation states in a particular sample. Ion chromatography (IC) [1] has become one of the most widely used analytical methods for the speciation of these elements due to its potentialities, as summarized in a review [2]. The main advantages of IC are the capability for speciation and, furthermore, on-line matrix elimination and sample preconcentration is possible using an appropriate column, which can lower the detection limits. A lot of research has been done to improve the detection limits in IC, where it is very important to efficiently separate particular species of heavy metals even when they are present in very low concentrations (below 1 μg dm^{-3}) [3].

One of the detection methods to improve the detection limits in IC is thermal lens spectrometry (TLS), which is known for its high sensitivity [4,5]. TLS is based on the indirect measurement of absorbance via the so-called thermal lens effect. This phenomenon is a result of the heat generated in an

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irradiated sample by the non-radiative relaxation of absorbed energy [6,7]. When a laser beam with a Gaussian profile is used as an excitation source, the energy deposited in the sample results in a characteristic Gaussian radial temperature distribution and in the corresponding refractive index gradient. A lens-like optical element is consequently formed within the irradiated sample and the initial intensity profile of the laser beam changes. The relative change in the laser intensity at the beam axis is a direct measure of the thermal lens strength, that itself is proportional to the sample's absorbance and the power of excitation beam. Furthermore, the magnitude of the thermal lens signal and the sensitivity of the technique depend on the thermooptical properties of the sample (such as $\partial n/\partial T$, the temperature coefficient of refractive index and k, the thermal conductivity) as given by Eq. (1):

$$\frac{\Delta I}{I} = \frac{2.303AP(-\partial n/\partial T)}{1.91\lambda k} = 2.303AE \quad (1)$$

where

$$E = \frac{P(-\partial n/\partial T)}{1.91\lambda k} \quad (2)$$

E represents the so-called enhancement factor compared to conventional transmission measurements, A is absorbance, P is the excitation laser power and λ is the probe laser wavelength.

The described dependence of the TLS signal on excitation laser power provides intrinsically high sensitivity and in principle lower limits of detection (LODs) of TLS compared to conventional spectrometry. The applicability of the TLS technique for sensitive on-line determination of Cr(III) and Cr(VI) after IC separation has already been demonstrated [8]. The performance of the TLS technique has also been verified by intercomparison analyses [9] and by determination of Cr(VI) in standard reference water samples [10]. The combination of TLS and IC was reported to provide LODs of 30 μg dm^{-3} for Cr(III) and 0.3 μg dm^{-3} for Cr(VI) [8], which is lower compared to IC with UV–Vis detection and comparable to inductively coupled plasma MS [11]. However, in the case of some environmental samples, such as drinking water in which the concentrations of chromium species [particularly Cr(III)] are usually very low [9], the LODs obtained by TLS are not always sufficient. This is partly due to the fact that an aqueous matrix, such as normally encountered in IC, is not the most favorable medium for TLS measurements.

From Eqs. (1) and (2), and from the $\partial n/\partial T$ and k values given in Table 1 [12,13], it can be calculated that in organic solvents such as acetonitrile, acetone or methanol, the sensitivity of TLS is at least an order of magnitude higher, compared to transmission techniques, when only 10 mW of laser power is used. Using solvents with low $\partial n/\partial T$ and high k (like water), the sensitivity can be more than 10 times lower, compared to TLS measurements in solvents with more favorable thermooptical properties. This has represented the limiting factor for the application of TLS in ion chromatography, where the detection of separated species is normally performed in aqueous medium. The addition of an organic solvent was possible only after the separation of species on the column, in the post-column reagent. The development of solvent-compatible IC separation columns (such as Dionex HPIC CS5A) has, however, permitted the use of modified aqueous eluents, containing organic solvents with lower thermal conductivities and higher temperature coefficients of refractive index than water. Enhancement of the TLS signal has been reported in the presence of water-soluble organic solvents in non-flowing aqueous samples [14]. The main objective of this work was to investigate the effects of added organic solvents (methanol, acetone and acetonitrile) on the sensitivity and detection limits of chromium species by IC–TLS determinations, and on their separation in the presence of organic solvents.

Table 1
Thermooptical properties of used solvents

Solvent	Thermooptical properties (20°C)		E (W^{-1})
	k ($W\,m^{-1}\,K^{-1}$)	$\partial n/\partial T$ ($10^4\,K^{-1}$)	
Water	0.598	−0.91	130
Acetonitrile	0.188	−4.50	1980
Acetone	0.190	−5.42	2360
Methanol	0.202	−3.94	1620

Enhancement factors, $E=(-\partial n/\partial T)/(1.91\lambda k)$, were calculated for 632.8 nm. Thermooptical properties were taken from Ref. [13].

2. Experimental

2.1. Reagents

Gradient-grade organic solvents (methanol, acetone and acetonitrile, all from Fluka) were used, while all other used reagents were of analytical grade.

The PDCA reagent solution consisted of 20 m*M* PDCA (pyridine-2,6-dicarboxylic acid), 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.

$Cr(NO_3)_3 \cdot 9H_2O$ in 0.5 *M* HNO_3 (Merck) was used as the Cr(III) stock solution (1.000 ± 2 g dm^{-3}) and Cr(VI) stock solution (1.000 g dm^{-3}) was prepared by dissolving 2.828 g of $K_2Cr_2O_7$ (analytical-reagent grade, min 99.8%, Riedel-de Haen) in 1 dm^3 of distilled water.

Cr(III) was converted into the $Cr(PDCA)_2^-$ complex after adjusting the pH of the Cr(III) solution to 4 (to avoid precipitation of chromium hydroxide at higher pH). Subsequently, 5 cm^3 of the Cr(III) stock solution were added to 10 cm^3 of PDCA reagent 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 cm^3 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 the corresponding stock solutions, organic solvents (the same amount as in the eluent) and water.

The post-column 1,5-diphenylcarbazide (DPC) reagent was prepared by dissolving 0.5 g of DPC in 100 cm^3 of CH_3OH, adding 500 cm^3 of diluted H_2SO_4 (25 cm^3 of 95% H_2SO_4 diluted to 500 cm^3 by distilled water), and diluting with distilled water to the volume of 1 dm^3.

2.2. Chromatographic conditions

The metal-free chromatographic system consisted of a Shimadzu HPLC pump (Model LC10Ai), a Rheodyne injection valve with 200 mm^3 sample loop, a HPIC CG5A (50×4 mm I.D.) guard column and a HPIC CS5A (250 mm×4 mm I.D.) separation column, both from Dionex, attached to the on-line post-column reactor, and further to the flow-through cell (Helma, volume 8 mm^3, path length 1 cm). The eluent containing 2 m*M* PDCA, 2 m*M* Na_2HPO_4, 1 m*M* NaI, 5 m*M* CH_3COONH_4 and 2.8 m*M* LiOH was prepared by 10-fold dilution of PDCA reagent solution with 18 MΩ deionized water and was delivered to the column at a flow-rate of 1.0 cm^3 min^{-1}. The post-column reagent was 2 m*M* DPC, 10% CH_3OH, 0.45 *M* H_2SO_4, delivered into the system at a flow-rate of 0.5 cm^3 min^{-1} by the Dionex pneumatic post-column reagent delivery module.

To improve the sensitivity of TLS detection, 20% of water in the eluent and 40% of water in post-column reagent were replaced by methanol or acetone. In the case of added acetonitrile, 30% of water in the eluent and 60% of water in post-column reagent were replaced.

2.3. Detection system

TLS measurements were performed on a dual-beam TLS instrument (Fig. 1) using an experimental setup with mismatched focusing of pump and probe beam similar to the instrument described previously [8]. An argon ion laser (Coherent, Innova 90), operating at 514.5 nm (160 mW at the sample site) was used as an excitation source (pump beam). The pump beam was modulated by a mechanical chopper (Scitec Instruments) at 75 Hz and focused onto the sample cell by a 100-mm focal length lens. A helium–neon laser (Uniphase, Model 1103P, 632.8

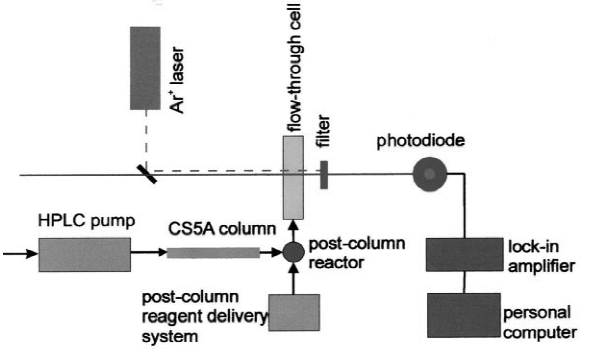

Fig. 1. Schematic diagram of the IC–TLS system, used in this work.

nm, 2 mW) provided the probe beam. Collinear propagation of the pump and probe beam was obtained by a dichroic mirror. The changes in the probe beam center intensity were detected with a silicon photodiode (Laser Components, OSD 5-E), which was connected to a lock-in amplifier (Stanford Research Systems, Model SR830, pre-set time constant of 3 s) and to the computer.

3. Results and discussion

As a preliminary test of the effect of organic solvent, a batch mode experiment was performed, following the standard procedure for determination of Cr(VI) with DPC [15]. Calibration curves were prepared in the concentration range of 1.0–20.0 μg dm^{-3}, with the addition of different amounts of acetone (0–30%). Differently from the experimental conditions, described in Section 2, the lock-in time constant was set to 1 s and the modulation frequency to 8 Hz. From the curves shown in Fig. 2, it is obvious that the sensitivity of the technique was increased with the addition of acetone. The sensitivity was increased up to 2.5 times and up to 3.3 times in the case of 20 and 30% acetone addition, respectively. In all cases, good linearity with regression coefficients (r^2) higher than 0.998 were observed, except with the addition of 30% acetone. In this case 'signal saturation' was reached at concentrations above 15 μg dm^{-3} under the described experimental conditions. This 'saturation effect' appears at high thermal lens strengths when the beam center intensity I approaches zero value and can therefore not be further decreased, not even by changing the parameters effecting the thermal lens strength (concentration, laser power, etc.). However, for lower concentrations, particularly those not accessible by conventional UV–Vis spectrometry (below 5 μg dm^{-3}), the TLS demonstrated acceptable linearity even for 30% acetone solution (regression coefficient 0.998).

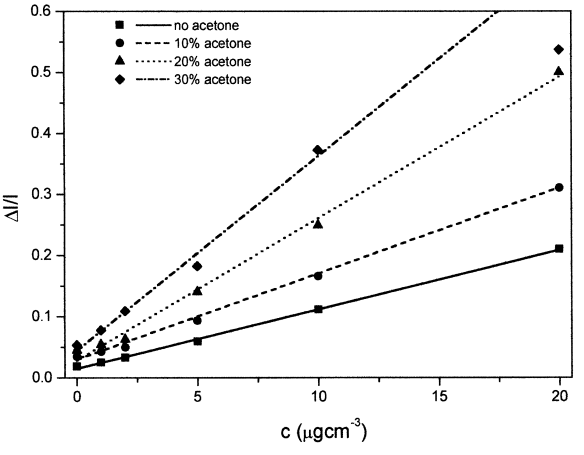

Fig. 2. Calibration curves for the batch mode Cr(VI)–DPC reaction with the addition of different amounts of acetone.

Based on the results obtained with the addition of acetone in the batch mode experiment, one can expect similar improvements in sensitivity in IC in which the LODs reported for TLS are still 3 times higher than those found for batch mode determination of Cr(VI) [8]. Therefore, the influence of added acetone or some other organic solvent on ion chromatography was investigated.

The solvents and their amounts used to study the effects on the sensitivity and on the chromatographic separation of Cr species were chosen on the basis of the thermooptical properties of the solvents and the manufacturers specifications about the solvent compatibility of the column [16]. The amounts of solvents used and the calculated enhancement factors are summarized in Table 2. In all cases the presence of methanol, resulting from the addition of the post-column reagent (10% methanol) was taken into account. Thermooptical parameters ($\partial n/\partial T$, k) for used mixtures of solvents are not available in the literature, therefore the exact enhancement factors could not be calculated. Instead, enhancement factors

Table 2
Enhancement factors, calculated for the eluent and different addition of used amounts of solvents

Added solvent	Addition of solvent (%)		E_{solv} (W^{-1})	E_{solv}/E_{eluent}
	In eluent	In DPC		
No addition	–	–	180	1.0
Acetonitrile	30	60	920	5.4
Acetone	20	40	770	4.3
Methanol	20	40	570	3.2

Enhancement factors for amount of solvent used, $E=(-\partial n/\partial T)/(1.91\lambda k)$, were calculated for 632.8 nm. Thermooptical properties were taken from Ref. [13].

were extrapolated from the values for pure solvents, assuming that they change linearly with the composition of the solvent. The effect of dissolved reagents and modifiers in the eluent on the enhancement factor was considered negligible due to their low concentration, since it has been demonstrated that electrolytes at concentrations below 0.1 *M* have little effect on the enhancement factor [17,18]. Unfortunately, the contribution of H_2SO_4 from the post-column reagent could not be derived since no data on thermooptical properties of H_2SO_4 are available. It is however estimated from the effects of other strong electrolytes [17,18], that the contribution of about 0.15 *M* H_2SO_4 (present after the addition of post-column reagent) to the calculated enhancements is less than 10%.

First, chromatograms were recorded with the addition of 20% acetone in the eluent and 40% in the post-column reagent (Fig. 3). Chromatograms with added acetone were compared to those without the addition of organic solvent. The observed enhancement in the TLS signals by a factor of 2.5 is similar to the enhancement obtained in batch mode experiments. At the same time chromatographic peaks are shifted; the Cr(III) peak from 220 to 155 s and the Cr(VI) peak from 295 to 335 s. Similar effects were noted also when methanol (20% in eluent and 40% in DPC) and acetonitrile (30% in eluent and 60% in DPC) were used (Fig. 3). The higher amounts of acetonitrile, compared to methanol and acetone, were used, because acetonitrile has poorer thermooptical properties than acetone, so 'signal saturation' was not observed. The enhancements of the signals due to thermooptical properties were also obvious and were 2-fold with addition of methanol and 3-fold with addition of acetonitrile. The retention times for Cr(III) were decreased from 220 to 185 s in the case of methanol addition and to 130 s in case of acetonitrile addition. On the other hand, the retention times for Cr(VI) increased from 295 to 305 s and to 350 s, when methanol and acetonitrile were used, respectively. The addition of organic solvent increases the hydrophobicity of the eluent and the solubility of the Cr(III)–PDCA complex in the mobile phase, which resulted in shorter retention times for Cr(III). On the contrary, the addition of an organic solvent reduces the Cr(VI) solubility in the eluent and its affinity for stationary phase is increased, therefore, the retention time of Cr(VI) is longer.

To evaluate the enhancements in the signals, and consequently the sensitivity and LODs, achieved by the addition of all applied solvents, the chromatograms of samples containing different amounts of Cr(III) (from 60 to 450 μg dm^{-3}) and Cr(VI) (from 0.5 to 5.0 μg dm^{-3}) were recorded. Chromatograms taken with acetonitrile addition are shown in Fig. 4.

The sensitivity of the technique for each particular addition of solvent was expressed as the slope of calibration line, separately for Cr(III) and Cr(VI). The correlation coefficients were larger than 0.994 in the case of Cr(III) and larger than 0.999 in the case of Cr(VI). The sensitivity was the highest when acetonitrile was added. Slopes of calibration lines

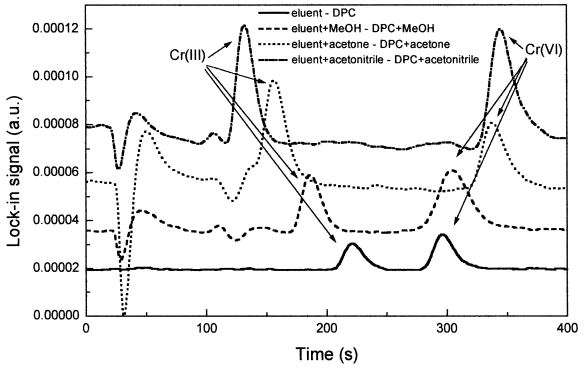

Fig. 3. Chromatograms of a mixture of 300 μg dm^{-3} of Cr(III) and 2.0 μg dm^{-3} of Cr(VI) with different organic solvents. For the sake of clarity, chromatograms are shifted vertically.

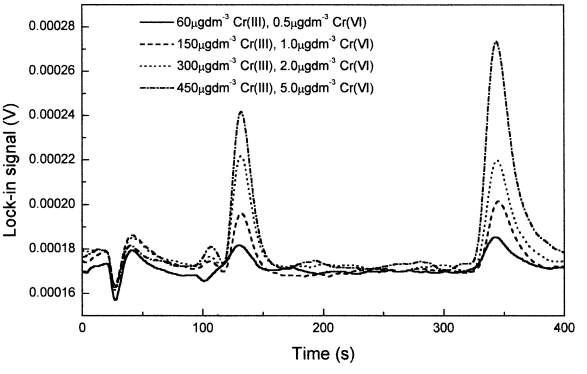

Fig. 4. Chromatograms of samples in 30% acetonitrile, obtained by the addition of acetonitrile to the eluent (30%) and post-column reagent (60%).

(Fig. 5) were compared to those of the standard procedure, without the solvent modification. From the comparison of the slope of the respective calibration lines with the slope of the calibration line without organic solvents added to the eluent and post-column reagent, the enhancements in sensitivity were calculated. The values obtained are summarized in Table 3 and they are in general lower than theoretically calculated values given in Table 2. Lower enhancement factors could be attributed to experimental errors (imperfect alignment of beams at the cell site) or to the fact that in our calculations the enhancement factors were extrapolated from thermooptical properties of pure solvents, and not calculated from thermooptical properties of the real mixtures used as eluent and post-column reagent.

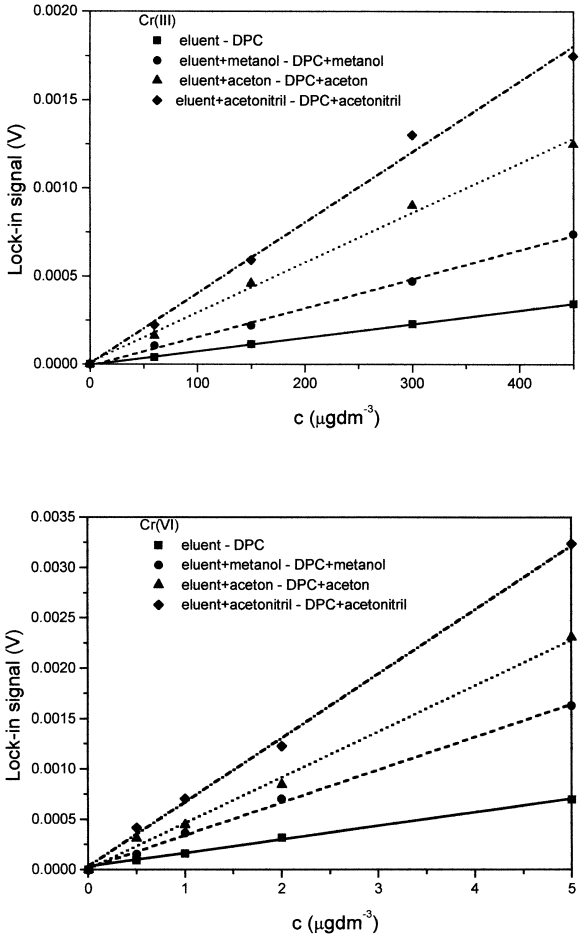

Fig. 5. IC–TLS calibration lines for Cr(III) and Cr(VI), obtained with various eluent/solvent combinations.

Table 3
Enhancement factors for Cr(III) and Cr(VI), calculated as slope of calibration line with added solvent against the slope of calibration line with no addition

Added solvent	Enhancement for:	
	Cr(III)	Cr(VI)
No addition	1.0±0.02	1.0±0.04
Acetonitrile	5.2±0.24	5.0±0.24
Acetone	3.6±0.15	3.4±0.13
Methanol	2.1±0.09	2.4±0.09

The detection limits, calculated from calibration lines ($S/N=3$ basis), were 10 μg dm^{-3} for Cr(III) and 0.1 μg dm^{-3} for Cr(VI). These values correspond to 2 ng of Cr(III) and 20 pg of Cr(VI) injected onto the IC column and represent a 3-fold improvement compared to previously reported values for IC–TLS [8].

The applicability of the method for real samples analysis was tested by determination of Cr(VI) in aqueous extracts of two lime-treated sewage sludge samples, which were also analyzed by electrothermal atomic absorption spectrometry (ET-AAS), following separation on an anion-exchange fast protein liquid chromatographic (FPLC) column [19,20]. For more realistic comparison to ET-AAS, only the fractions containing Cr(VI) was analyzed by IC–TLS, even though the lime-treated sewage sludge extracts could be injected on the IC column. Fractions (0.5 cm^3) were collected throughout the FPLC chromatographic run. Cr(VI) was contained in the 12.5-min fraction, which was analyzed by IC–TLS with the addition of acetone or acetonitrile and also by ET-AAS. The results presented in Table 4 show excellent agreement when acetonitrile was added (sample B), while the deviation is higher (up to 10%)

Table 4
Comparison of results obtained by TLS and ET-AAS

Sample	Added solvent in IC	Cr(VI) conc. measured by:	
		TLS (μg dm^{-3})	ET-AAS (μg dm^{-3})
A	Acetone	15.2±0.4	16.9±0.9
B	Acetonitrile	10.7±0.3	11.0±0.7

for sample A, which was analyzed following the addition of acetone.

4. Conclusions

It has been demonstrated that the addition of acetone in the batch mode determination of Cr(VI) improves the sensitivity of the TLS method. Similarly, the addition of organic solvents to the eluent and post-column reagent enhances the TLS signal and the sensitivity of detection in ion chromatography. Among the solvents used (methanol, acetone and acetonitrile) the enhancement was the highest in the case of acetonitrile addition. The sensitivity of the technique was improved up to 3 times compared to IC–TLS determination of chromium species in water based solutions and LODs of 10 and 0.1 μg dm^{-3} for Cr(III) and Cr(VI), respectively, were achieved. The added solvents also influence the Cr(III)/Cr(VI) separation by changing the retention times of the individual peaks (Cr(III) to shorter and Cr(VI) to longer retention times).

Additional verification of the method was performed by comparison of the results obtained by IC–TLS with solvent addition, to an independent analytical technique, such as ET–AAS. The agreement of the results revealed the suitability of the method for determination of chromium species in routine analysis.

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