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Interfacing ion chromatography with inductively coupled plasma atomic emission spectrometry for the determination of chromium(III) and chromium(VI)

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Abstract

Cr(III) and Cr(VI) can be separated and detected by ion chromatography (IC) with inductively coupled plasma atomic emission spectrometry (ICP-AES). This combined method gives reliable, reproducible results rather quickly. A measurement requires 3 min and a 50-μl sample. ICP-AES was used as an element-selective detection method for IC. Two IC techniques were compared for separation. In the first case the eluent was 7.5 m*M* potassium hydrogenphthalate and in the second case eluent changing was used. The first eluent was water; the second was 1 *M* HNO_3. The IC column was a Polispher AN anion exchanger. The Cr(VI) (CrO_4^{2-}, $Cr_2O_7^{2-}$) is retained in the column while the Cr(III) passes through without any retention. The main advantages of ICP detection are: the first (eluent) peak —which contains the Cr(III)— can be evaluated and the element selectivity and sensitivity provides reliable results. These methods were used for measuring the water-soluble Cr(III) and Cr(VI) contents of contaminated soils. The detection limits of Cr(III) and Cr(VI) are 0.25 and 0.27 μg/g, respectively.

1. Introduction

The concentration measurement of any ionic form can be particularly important in environmental samples when one ionic form (oxidation state) of the examined element is much more poisonous than the other(s). This is true in the case of chromium too.

Hexavalent chromium (CrO_4^{2-}, $Cr_2O_7^{2-}$) is very toxic and carcinogenic [1]; however, inorganic chromium(III) is essential for mammals [2]. Only atomic absorption or plasma atomic emission techniques provide information on the total amount of chromium in a test solution. This is the reason several approaches have been tried for the chromium speciation.

By means of industrial contamination through fertilization and the application of sewage sludge to arable land, a considerable quantity of chromium can get into soil and from here into surface water. In existing studies, the total amount of chromium in water, soil and plant samples was often measured with either atomic absorption spectrophotometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES) in the older studies. The degree of real danger could not be determined from the data obtained with the above methods.

The oxidation states of chromium were measured separately by using one of the following approaches: (i) after organic extraction sepa-

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ration of the two oxidation forms with AAS [3], (ii) with a photometer, using 1,5-diphenylcarbazide [4], (iii) by selectively volatilizing chromium species in a graphite furnace [5], (iv) by flow injection with UV detection [6], (v) by flow injection–AAS [7–9], (vi) by flow injection ICP-AES [10], (vii) by high-performance liquid chromatography (HPLC) and UV detection [11–14], (viii) by HPLC with electrochemical detection [15], (ix) by HPLC–AAS [16], (x) by HPLC–direct current plasma (DCP) [17,18], (xi) by HPLC–ICP-AES [19].

The extraction procedures are difficult. In photometric measurements there are some problems because of the effect of interfering elements (e.g. Fe(III) [20]) in the solution. The greatest sensitivity, precision, rapidity and reproducibility can be expected with the application of either flow injection (FIA) or HPLC linked to either AAS or ICP-AES instruments.

Either an acidic or a basic activated aluminium oxide, a reversed-phase C_{18} column or an ion-exchange column is used for the separation of chromium(III) and chromium(VI) in the FIA and HPLC analyses. Either AAS or ICP-AES instruments are used as an element-selective detection method. With the above-mentioned combined methods the analyses of Cr(III) and Cr(VI) can be of appropriate sensitivity.

2. Experimental

2.1. ICP-AES

A Labtam 8440M ICP-AES system with a mono- and polychromator (Labtam, Melbourne, Australia) was used. The polychromator of the ICP-AES system is a vertically mounted Paschen–Runge design with a 1-m focal length, 60 channel places and vacuum operation. The radio frequency generator is crystal controlled, operating at 27.12 MHz. A stop-flow GMK nebulizer (Labtam) is used. The following conditions were used: sample gas pressure 280 kPa; sample gas flow-rate 4.1 l/min; coolant gas pressure 140 kPa; coolant gas flow-rate 4 l/min; auxiliary gas pressure 100 kPa; auxiliary gas flow-rate 2.5 l/min; flushing gas flow-rate 1 l/min; forward power 1400 W; reflected power 5 W; ICP-AES wavelength 267.716 nm. BDH (Poole, UK) standards ($CrCl_3$ 1 mg/ml) and Reanal (Budapest, Hungary) analytical-reagent grade solid chemicals (K_2CrO_4, $K_2Cr_2O_7$) were used to prepare the calibration solutions. The IC–ICP-AES calibration curves were adjusted by measuring a high and a low standard every day.

2.2. IC

A Merck–Hitachi (E. Merck, Darmstadt, Germany) L-6200A HPLC pump with a Polyspher IC AN anion-exchange column (pre-packed column RT 100-3,2 Cat. 19815) was used in the experiments described. Two sets of conditions were applied: *Method I*: mobile phase 7.5 m*M* potassium hydrogenphthalate with 5 g/l ethylene glycol and 40 g/l 2-propanol added; flow-rate 4 ml/min; pressure 40 bar; injection volume 50 μl; measurement time 4–5 min. Retention times were 0.5 min (28 s) for Cr(III) and 2 min (119 s) for Cr(VI). *Method II*: mobile phase A, water; mobile phase B, 1 *M* HNO_3; gradient: A from 0 to 36 s, B from 36 to 120 s, followed by an abrupt change to A after 120 s; flow-rate 4 ml/min; pressure 67 bar; injected volume 50 μl; measurement time 3 min. Retention times were 0.5 min (28 s) for Cr(III) and 2 min (133 s) for Cr(VI).

All chemicals used were purchased from Reanal and were of the highest purity available. Double-distilled water was used in preparing the mobile phases.

3. Results and discussion

3.1. Optimizing of IC and ICP-AES parameters

First the IC flow-rate was optimized. Our stop-flow GMK nebulizer, a V-grove, modified Babington nebulizer, requires a relatively high flow-rate. The flow-rate–signal intensity function is a saturation curve (Fig. 1). Our aim was to reach

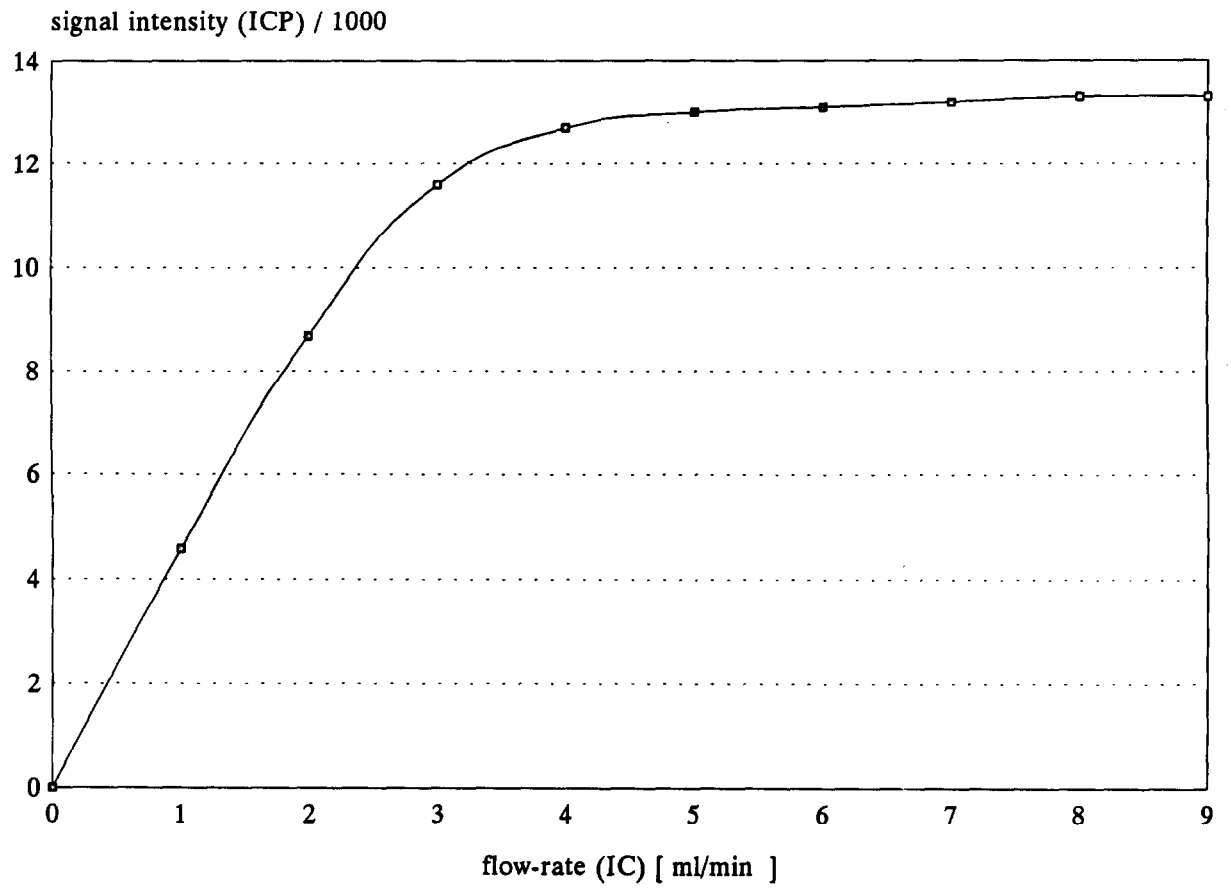

Fig. 1. Optimizing the IC flow-rate. The introduced solution was potassium hydrogenphthalate. The HPLC pump was linked to the ICP-AES system trought the stop-flow GMK nebulizer. The intensity of the ICP-AES signal was measured at 766.490 nm, on the line of potassium.

the highest intensity at the lowest flow-rate. Therefore the optimum value is 4 ml/min.

There is another way to increase the signal intensity: increasing the pressure of the sample gas. On the other hand, increasing the flow-rate of the sample gas increases the background intensity as well. The optimal pressure value is at the highest signal/background ratio, because the background equivalent concentration (BEC) is the lowest here. The pressure optimum is 280 kPa (Fig. 2).

Two separation methods were compared. The column was a Polispher AN anion-exchange column in both cases. In the first separation method the mobile phase was 7.5 m*M* potassium hydrogenphthalate. In this case the chromium(III) is in the solution peak, because it is a cation. The second peak on the chromium line is chromium(VI) (Fig. 3.) because it behaved as CrO_4^{2-} anion. There is no difference between the retention time of CrO_4^{2-} and the $Cr_2O_7^{2-}$ anions. The starting point for eluent development was the suggested eluent composition for the anion (Cl^-, NO_3^-, SO_4^{2-}, etc.) separation. This eluent contains 0.75 m*M* potassium hydrogenphthalate, 5 g/l ethylene glycol and 40 g/l 2-propanol. Using this eluent, the retention time for chromium(VI) was more than 50 min. Increasing the concentration of potassium hydrogenphthalate decreased the retention time. Our aim was to obtain a short separation time (3–5 min). The selected eluent (7.5 m*M* potassium hydro-

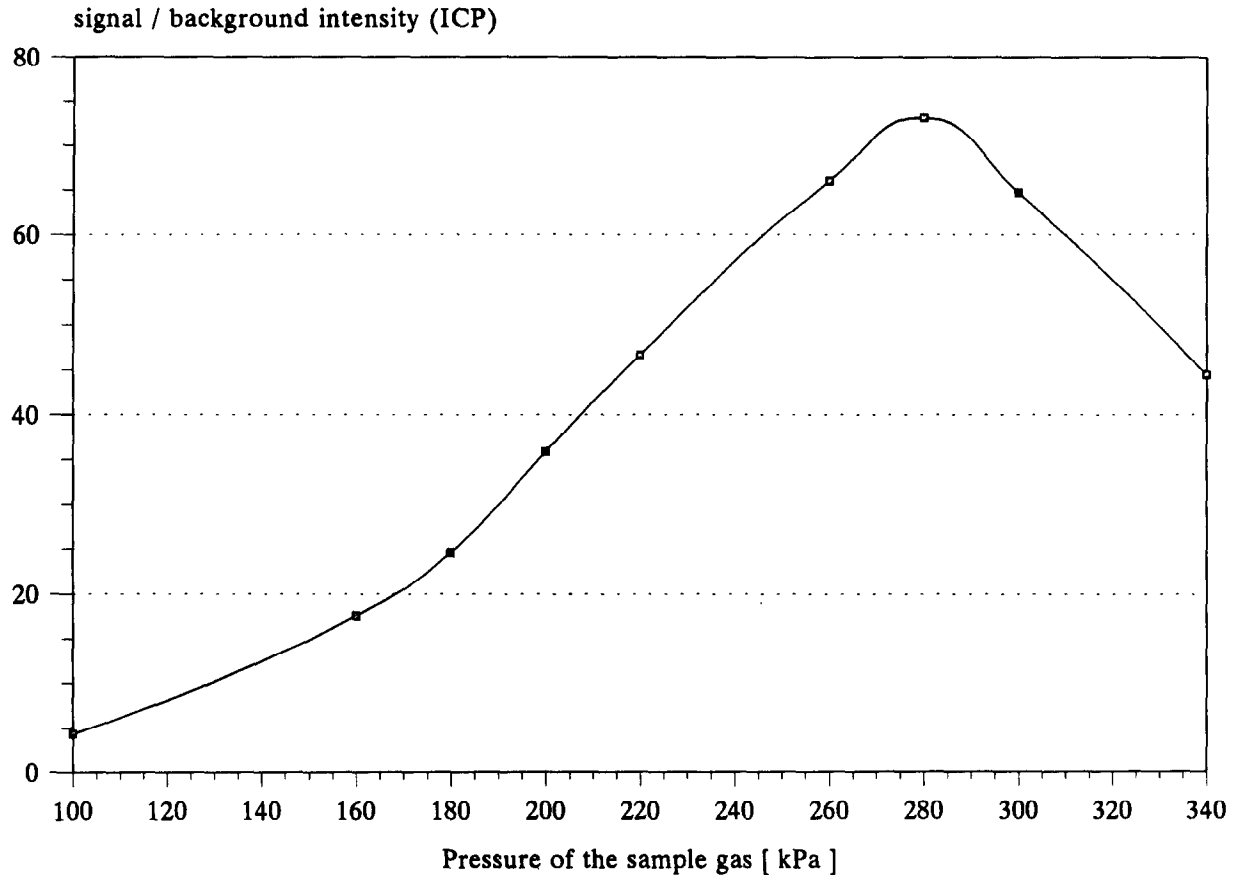

Fig. 2. Optimizing of the ICP-AES sample gas pressure. The test solution was 100 mg/kg Cr(III) solution. The optimal pressure is at the highest signal/bakground ratio.

genphthalate with 5 g/l ethylene glycol and 40 g/l 2-propanol) yielded a satisfactory result.

A second separation method was also studied. Two eluents and a stepped gradient were applied. The eluent changing was controlled with a gradient HPLC pump. Eluent A was distilled water. In the first step the chromium(III) went through the anion-exchange column without any adsorption and all chromium(VI) anions were retained in the column. After 36 s the pump changed eluent. Eluent B, 1 *M* HNO_3 removed all absorbed anions from the column (Fig. 4.). We obtained a peak only at 2 min because of the volume between the pump and the loop. After 2 min the pump changed back to eluent A. The detection limits (at 3σ) for chromium(III) are the same for the first and second methods, 0.25 μg/ml. However, there is a difference between the detection limits of chromium(VI) using methods I (1.0) and II (0.27 μg/ml). The reproducibilities of both methods were less than 2% R.S.D.

These methods are suitable for measuring the water-soluble chromium(III) and chromium(VI) content of contaminated soils, waste waters and sewage sludge.

The total amount of chromium (measured by ICP-AES) and the sum of the Cr(III) and Cr(VI) contents were compared as well. The differences were less than 3%.

The calibration curves were determined with BDH and Reanal standard solutions. For each separation method the calibration chromatograms are shown in Figs. 5–8. The calibration

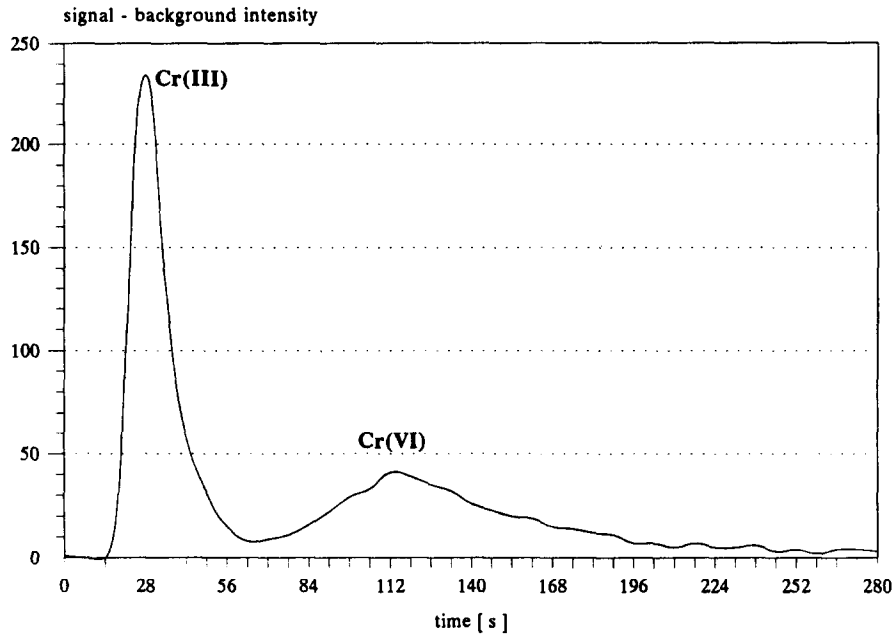

Fig. 3. Chromatogram of 10 μg/g chromium(III) and 10 μg/g chromium(VI) standard solution with method I. Eluent: 7.5 m*M* potassium hydrogenphthalate, flow-rate 4 ml/min, ICP-AES detection at 267.716 nm.

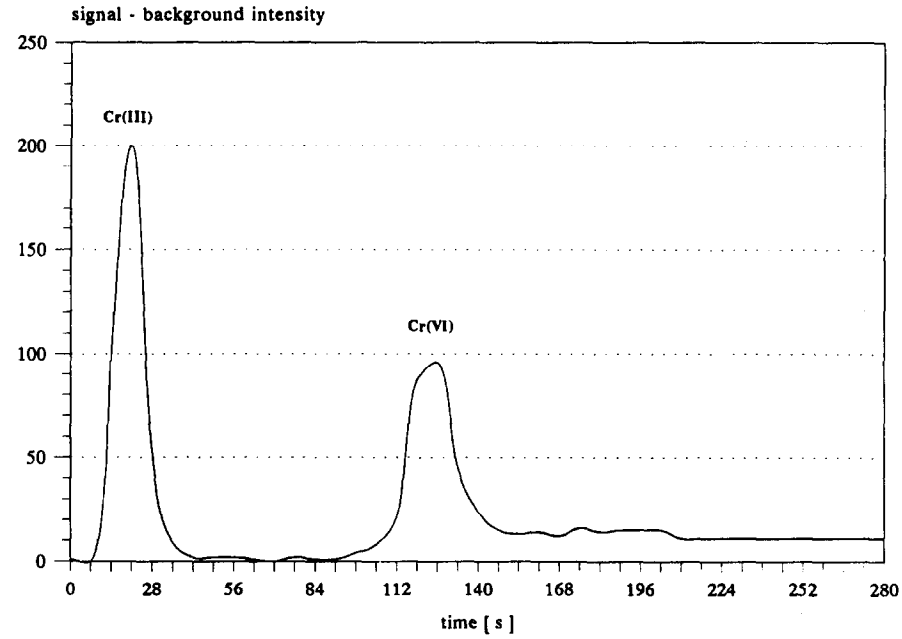

Fig. 4. Chromatogram of 10 μg/g chromium(III) and 10 μg/g chromium(VI) standard solution with method II. Gradient elution was applied. Eluent program 0–36 s water, 36–120 s 1 *M* HNO_3 followed by abrupt change to water after 120 s. Flow-rate 4 ml/min, ICP-AES detection at 267.716 nm.

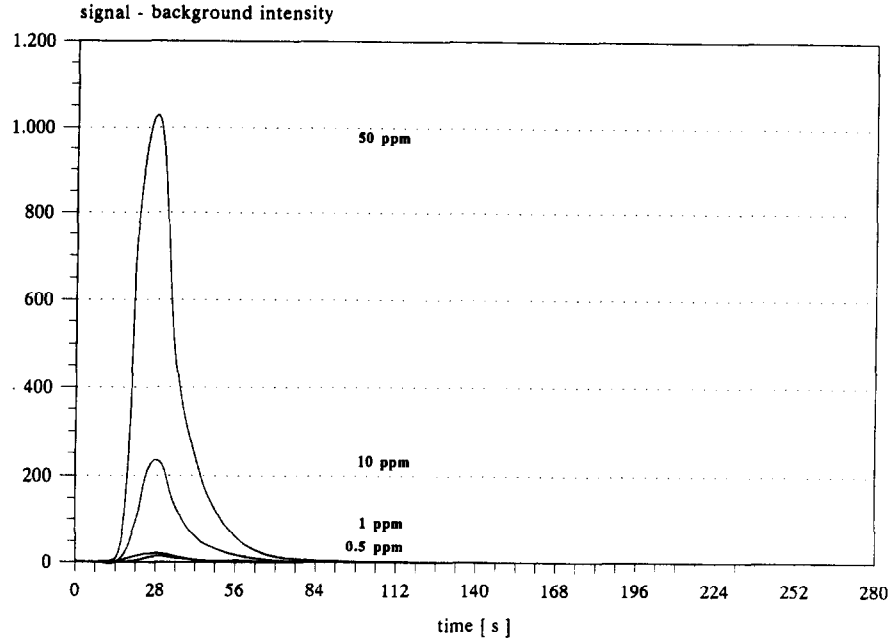

Fig. 5. Chromatograms of chromium(III) standard solutions for the calibration with method I (ppm = mg/kg). Conditions as in Fig. 3.

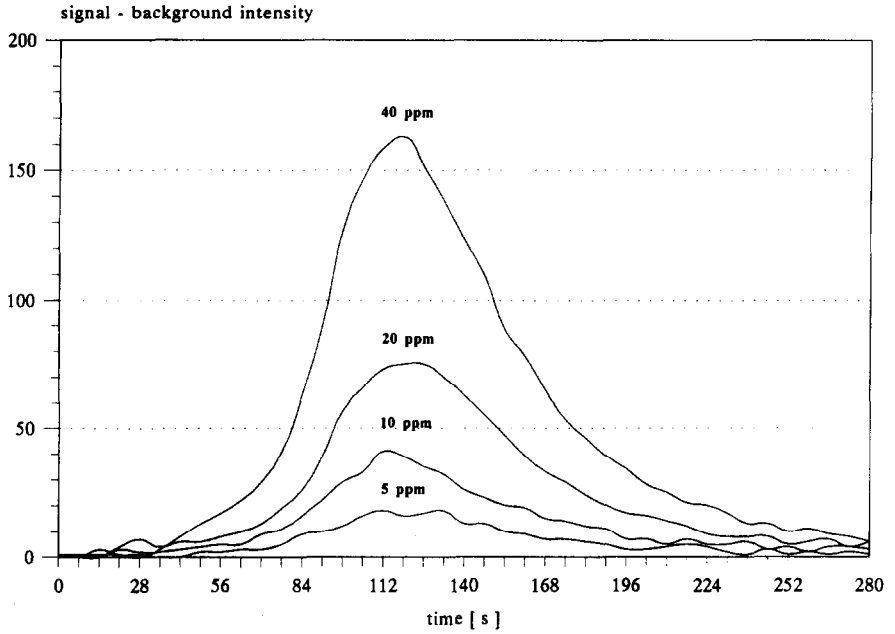

Fig. 6. Chromatograms of chromium(VI) standard solutions for the calibration with method I. Conditions as in Fig. 3.

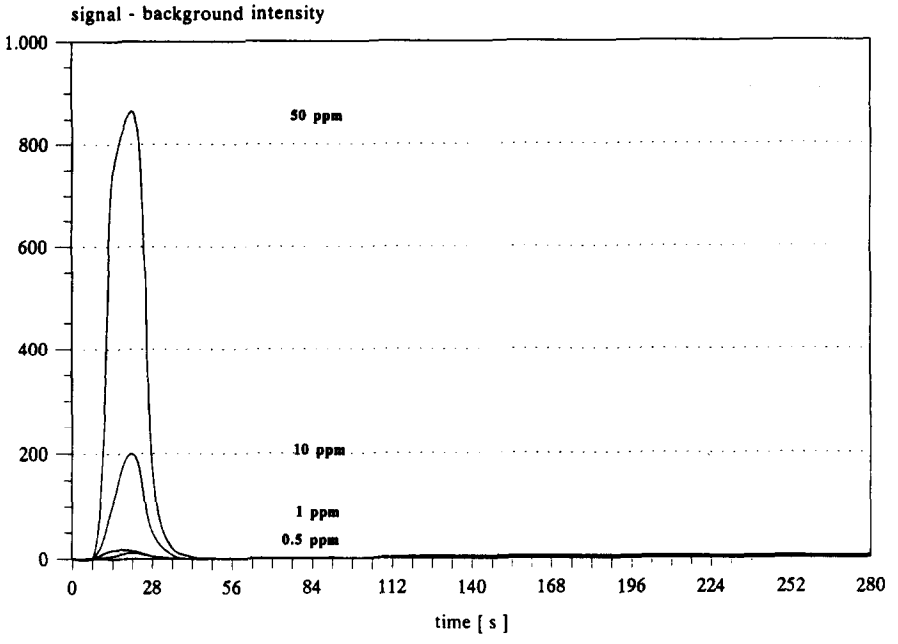

Fig. 7. Chromatograms of chromium(III) standard solutions with method II. Conditions as in Fig. 4.

equations are in Table 1 (based on the peak height). The calibration curves are linear in the 0–40 μg/ml concentration range for both chromium(III) and chromium(VI).

3.2. Long-term stability of the column

The Polispher IC AN column was used for a year only for the speciation of chromium with

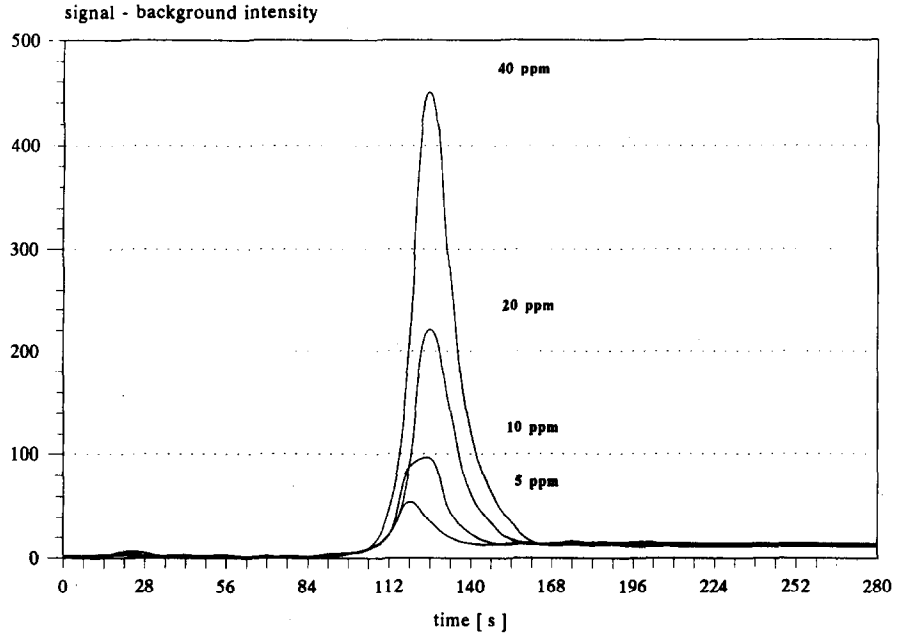

Fig. 8. Chromatograms of chromium(VI) standard solutions with method II. Conditions as in Fig. 4.

Table 1
Comparing the data of calibration curves $y = a + bx$

Ion	Method	a	b	r^2
Cr(III)	I	7.43	20.52	0.9992
Cr(III)	II	5.84	17.28	0.9990
Cr(VI)	I	0.00	4.36	0.9994
Cr(VI)	II	−4.65	11.07	0.9984

these two methods. We did not find any changes in the measurements of either chromium form. Changes in the theoretical plate number of the column were also estimated for the nitrate ion (with conductivity detection). It decreased to 70% of the original value by the end of the year. From this time onward the column was used only for chromium separation with method II, because decreases of the theoretical plate number have no effect on the efficiency of this method.

3.3. Data acquisition

The original ICP-AES software was used for data collection. The integration time was 5 s, with sufficiently low background noise ($\sigma = 1.12$)

3.4. Recovery from soil samples

Recovery of the entire amount of added chromium(VI) and chromium(III) from the soil samples is very difficult, because Cr(VI) oxidizes the organic matter in the soil and Cr(III) adsorbs at the surface of soil. The rate of oxidation depends on the pH and humus content. In the first few minutes the Cr(VI) content starts to decrease. The rate of this reaction varies for different soils. In our experiments 20 ml of a 100 μg/ml Cr(VI) solution was added to 20 g air dried soil samples. After 30 min shaking the samples were filtered and the Cr(VI) concentration was measured. Studying two soil types for 30 min after the chromium addition, the recoveries from neutral chernozem and sandy soil were 96.7 and 98.6%, respectively. When we added acidic (pH 3) Cr(VI) solution to these soils the recoveries from the chernozem and sandy soil were 42.9 and 77.0%, respectively. After 24 h shaking in the case of neutral Cr(VI) the concentrations of Cr(VI) in the filtered solution decreased to 70.9 and 88.5% for the chernozem and sandy soil respectively. When we used acidic Cr(VI) solution and it was shaken for 24 h, 9.74 and 32.8% recovery rates were obtained for the chernozem and sandy soil, respectively. This result shows that Cr(VI) can be measured exactly only in near-neutral soils by using a short shaking time.

References

[1] F. Borguet, R. Cornellis and N. Lameire, *Biol. Trace Elem. Res.*, 26 (1990) 449.
[2] H. Salem and S.A. Katz, *Sci. Total Environ.*, 86 (1989) 59.
[3] K.S. Subramanian, *Anal. Chem.*, 60 (1988) 11.
[4] H. Marchart, *Anal. Chim. Acta*, 30 (1964) 11.
[5] S. Arpadjan and V. Krivan, *Anal. Chem.*, 58 (1986) 2612.
[6] A.N. Araujo, J.L.F.C. Lima and A.O.S.S. Rangel, *Analyst*, 114 (1989) 1465.
[7] A.G. Cox, I.G. Cook and W. McLeod, *Analyst*, 110 (1985) 331.
[8] M. Sperling, X. Yin and B. Welz, *Analyst*, 117 (1992) 629.
[9] M. Sperling, S. Xu and B. Welz, *Anal. Chem.*, 64 (1992) 3101.
[10] A.G. Cox and C.W. McLeod, *Anal. Chim. Acta*, 179 (1986) 487.
[11] X. Yao, J. Liu, J. Cheng and Y. Zeng, *Chem. Res. Chin. Univ.*, 7 (1991) 37.
[12] J. Jen, G. Ou-Yang, C. Chen and S. Yang, *Analyst*, 118 (1993) 1281.
[13] T. Tande, J.E. Pettersen and T. Torgrimsen, *Chromatographia*, 13 (1980) 607.
[14] E. Eijarvi, H.J. Lajunen and M. Heikka, *Finn. Chem. Lett.*, (1985) 227.
[15] A.M. Bond and G.G. Wallace, *Anal. Chem.*, 54 (1982) 1706.
[16] A. Syty, R.G. Christensen and T.C. Rains, *J. Anal. At. Spectrom.*, 3 (1988) 193.
[17] I.S. Krull, K.W. Panaro and L.L. Gerschman, *J. Chromatogr. Sci.*, 21 (1983) 460.
[18] I.T. Urasa and S.H. Nam, *J. Chromatogr. Sci.*, 27 (1989) 30.
[19] I.S. Krull and D. Bushee, *Anal. Lett.*, 15 (1982) 267.
[20] R. Milacic, J. Stupar, N. Kozuh and J. Korosin, *Analyst*, 117 (1992) 125.