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DETERMINATION OF CHROMIUM(VI) AND COMMON INORGANIC ANIONS IN INDUSTRIAL WASTEWATER BY MEANS OF SUPPRESSED ION CHROMATOGRAPHY

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OZNACZANIE CHROMU(VI) I GŁÓWNYCH ANIONÓW NIEORGANICZNYCH W ŚCIEKACH PRZEMYSŁOWYCH METODĄ CHROMATOGRAFII JONOWEJ Z TŁUMIENIEM PRZEWODNICTWA

Do jednoczesnego rozdzielania i oznaczania chlorków, azotanów, siarczanów i chromianów w ściekach przemysłowych zastosowano izokratyczną chromatografię jonową z detekcja konduktometryczną. Rozdzielanie przeprowadzono za pomocą kolumny anionowymiennej i eluentu $Na_2CO_3/NaHCO_3$ oraz pętli wstrzykowej o pojemności $20 \cdot 10^{-6}$ dm^3. Zakres liniowości dla chromianów sprawdzono od granic wykrywalności do 30 mg/dm^3. Granice wykrywalności jonów Cl^-, NO_3^-, SO_4^{2-} i CrO_4^{2-} były odpowiednio na poziomie: 1,18 mg/dm^3, 0,31 mg/dm^3, 1,74 mg/dm^3 i 0,63 mg/dm^3. Średni odzysk oznaczanych anionów w wzbogacanych próbkach był w zakresie od 87% do 109%, a wartość RSD nie przekraczała 4,67%.

Summary

Isocratic ion chromatography with suppressed conductivity detection was used for the simultaneous separation and determination of chloride, nitrate, sulfate and chromate in industrial wastewater. The separation was performed on an anion-exchange column with $Na_2CO_3/NaHCO_3$ eluent and $20 \cdot 10^{-6}$ dm^3 injection loop. Linearity of chromate was checked up to 30 mg/dm^3. The detection limits of Cl^-, NO_3^-, SO_4^{2-} and CrO_4^{2-} were on the levels: 1.18 mg/dm^3, 0.31 mg/dm^3, 1.74 mg/dm^3, and 0.63 mg/dm^3, respectively. The mean recoveries of target anions for spiked samples were 87–109% and accuracy did not exceed 4.67%.

INTRODUCTION

Analysis of wastewater is an important part of the environmental analysis. There is a need for strict control and monitoring of many substances present in water and wastewater in order to prevent contamination and protect the environment. The majority of disposed wastes, including recyclable waste, are not environmentally safe. The presence in sewage sludge of excess levels of potentially toxic elements, such as chromium, could affect the ability to recycle these residues in the future.

The use of chromium in many industrial activities such as tanning, plating and stainless steel welding results in a substantial disposal of sludges. Moreover, chromium contaminates soil and underground waters and ultimately enters the food chain.

In many laboratories within routine analysis the most frequently determined are inorganic ions and metals. Metals are usually determined by atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) methods. An essential tool for the analytical chemist, especially in the area of anion and cation analysis, is ion chromatography [8]. In many cases, this method has been used to replace conventional wet chemical methods, which are labor-intensive, time-consuming and occasionally susceptible to interferences.

It is noteworthy that some metals exist in environment in ionic forms. According to Das *et al.* [3] the most often determined metal in aqueous solutions is chromium.

The different toxicities and bioavailabilities of Cr(III) and Cr(VI) are public health concern and therefore require strict control. Trivalent chromium is essential for humans, where it is involved in glucose, lipid and protein metabolism, whereas the deleterious effects on living organism of Cr(VI) are well documented [7].

The hexavalent species exist primarily as the chromate CrO_4^{2-} or dichromate $Cr_2O_7^{2-}$ ion, depending upon the pH of solution. In either state, Cr(VI) is a strong oxidizer and therefore harmful for environmental and biological systems [2].

Most environmental analytical procedures for chromium determine Cr(III) and total chromium, and then basing on the difference, calculate the Cr(VI) content. Conventionally, colorimetric method has been used in the analysis of Cr(VI). Recently, hyphenated techniques have successfully replaced the older classical methods.

Analytical techniques routinely used to measure total chromium and the methodologies developed over the past several years for the analysis of Cr(VI) in environmental media are: ASTM Method D5281 for air; SW-846 Methods 3060A, 7196A, and 7199 for soils, sediments, and solid waste; and US EPA Methods 218.6 and 1636 for water [11].

Many detection protocols of chromium have been utilized including flame atomic absorption spectrometry (F AAS) [9], electrothermal atomic absorption spectrometry (ET AAS) [6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [1], and even liquid chromatography with chemiluminescence detection (LC-CL) [5], capillary electrophoresis with inductively coupled plasma mass spectrometry (CE-ICP MS) [13] and capillary electrophopresis with chemiluminescence detection (CE-CL) [12].

These methods are very useful for trace level determination and species analysis in low contaminated water samples. Nevertheless, hyphenated techniques require expensive instrumentation and are not available in routine laboratories.

Most laboratories use simply ion chromatography with conductivity detector systems for anion and cation analyses, and atomic absorption spectrometry for heavy metal determinations, which are cheaper, more convenient and sufficient for routine analysis.

The aim of the present work is application of isocratic ion chromatography with carbonate/bicarbonate eluent and suppressed conductivity detection for the simultaneous separation and determination of common inorganic anions (chloride, nitrate and sulfate) and chromate ions in industrial wastewater samples.

EXPERIMENTAL

Ion chromatographic separations were performed on Metrohm ion chromatography system (Herisau Metrohm AG, Switzerland) consisting of: 818 IC Pump, 837 IC Eluent Degasser, 830 IC Interface, 820 IC Separation Center, Rheodyne injection valve, Metrodata 2.3 software, autosampler (838 Advanced Sample Processor), MSM suppressor, and conductivity detector (819 IC).

Na_2CO_3, $NaHCO_3$ of analytical grades used for eluent preparation and 95% H_2SO_4 as a regenerant solution were obtained from Fluka (Fluka, Steinheim, Switzerland). NaCl, $NaNO_3$, and Na_2SO_4 of analytical grades were purchased from Fluka (Fluka, Steinheim, Switzerland). K_2CrO_4 was obtained from Merck (Merck, Darmstad, Germany).

Reference standard solution (AccuIon™, NIST, USA) containing Cl^- (30 mg/dm^3), NO_3^- (100 mg/dm^3) and SO_4^{2-} (150 mg/dm^3) was used for recovery test. For Cr(VI) recovery a standard solution was used.

Water used in the experiments was purified using Millipore equipment (Millipore, Bedford, MA, USA) and had an electrical conductivity of 0.05 μS/cm.

The stock solutions (1 000 mg/dm^3) were prepared by dissolving appropriate amount of suitable salts in deonized water. Stock solutions were stored in refrigerator and were stable for at least 3 months. Calibration solutions were prepared by diluting the standard solutions to the required concentration just before use, and were kept in polyethylene flasks at + 4°C.

RESULTS AND DISCUSSION

Method optimization

The ion chromatographic method used was adapted from a Dionex Technical Note no. 24 [4]. The divalent chromate anion was detected by suppressed conductivity after selective separation on appropriate ion-exchange stationary phase. This method allows for the simultaneous separation and determination of other anionic species in the sample, such as chloride, nitrate and sulphate.

Several ion-exchange columns were examined. The choice of anion-exchange columns resulted from the necessity of proper resolution between common inorganic anions and chromate which is highly polarizable ion and in this connection expected retention time is long. Nevertheless, the total analysis time should not be over reasonable time range. The separation columns used in the optimization process are listed in Table 1.

Table 1. The characteristic of ion-exchange columns used

Column	IonPac CS5A	IonPac AS5	IonPac AS9-SC	IonPac AS14	Anion Dual 2
Manufacturer	Dionex (Dionex, Sunnyvale, USA)				Metrohm (Herisau, Switzerland)
Column dimensions [mm]	4 x 250	4 x 250	4 x 250	4 x 250	4.6 x 75
Material	PS/DVB with bilayer of anion- and cation-exchange latex	PS/DVB with latex agglomerated anion exchange		EVB/ DVB	Polymethacrylate
Diameter [μm]	9	15	13	9	6
Cross-linking [%]	55	2	55	55	55
Organic solvents compatibility [%]	< 50	< 3	100	100	< 20
Capacity [μeq/column]	40 (anion exchange), 20 (cation exchange)	20	35	65	34
pH range	0–14	0–14	2–11	2–11	1–11

PS/DVB - Polystyrene/Divinylbenzene
EVB/DVB - Ethylenodivinylobenzene/Divinylbenzene

Two carbonate/bicarbonate eluents concentrations: 3.5 mM Na_2CO_3 + 1.0 mM $NaHCO_3$ (eluent I) and 5.0 mM Na_2CO_3 + 1.0 mM $NaHCO_3$ (eluent II) were used. The column oven was maintained at 32 °C. Samples were injected using $20 \cdot 10^{-6}$ dm^3 loop injector.

A standard solutions containing 10 mg/dm^3 of chromate in tap water was used for testing of five separation columns. The retention times (mean from triplicate analyses) of chloride, nitrate, sulphate and chromate in dependence on eluent used, obtained for each separation column, are given in Table 2. An examples of chromatogram obtained using Dionex IonPac AS14 separation column is shown of Figure 1.

Table 2. Mean retention times for analyzed anions (n = 3)

Eluent	Anions			
	Cl^-	NO_3^-	SO_4^{2-}	CrO_4^{2-}
IonPac CS5A				
I	3.83	6.79	13.74	11.96
II	3.56	6.02	9.82	10.53
IonPac AS5				
I	2.92	4.21	6.88	23.23
II	2.45	3.41	4.73	14.93
IonPac AS9-SC				
I	2.89	4.25	7.28	19.14
II	2.61	3.82	5.38	13.24
IonPac AS14				
I	6.07	9.66	16.02	27.34
II	5.49	8.69	11.67	19.27
Anion Dual 2				
I	3.27	4.19	6.06	10.53
II	2.90	3.69	4.47	7.38

All columns used in optimization procedure allow for simultaneous separation of Cl^-, NO_3^-, SO_4^{2-} and CrO_4^{2-} ions. Taking into consideration peak shapes and total retention times, which should not be too long, the best chromatographic performances proved Dionex IonPac AS14 with connection of a suitable guard column, and 5.0 mM Na_2CO_3 + 1.0 mM $NaHCO_3$ eluent with a flow rate of 0.7 cm^3/min. These analytical conditions were used in further study.

The elution order of analyzed anions was consistent with ion exchange rules (Cl^-, NO_3, SO_4^{2-} and CrO_4^{2-}) except for bifunctional Dionex IonPac CS5A column. In that case chromate ions were eluted before sulphate ions as is shown in Figure 2.

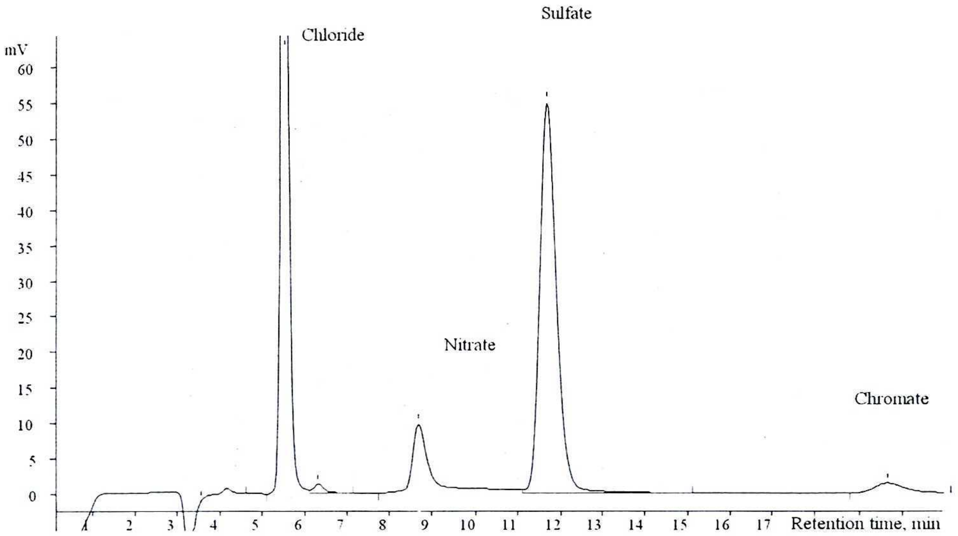

Fig. 1. Chromatogram of chromate standard (10 mg/dm^3) in tap water
Column – Dionex IonPac AS14
Eluent – 5.0 mM Na_2CO_3 + 1.0 mM $NaHCO_3$,
Detection – Suppressed conductivity

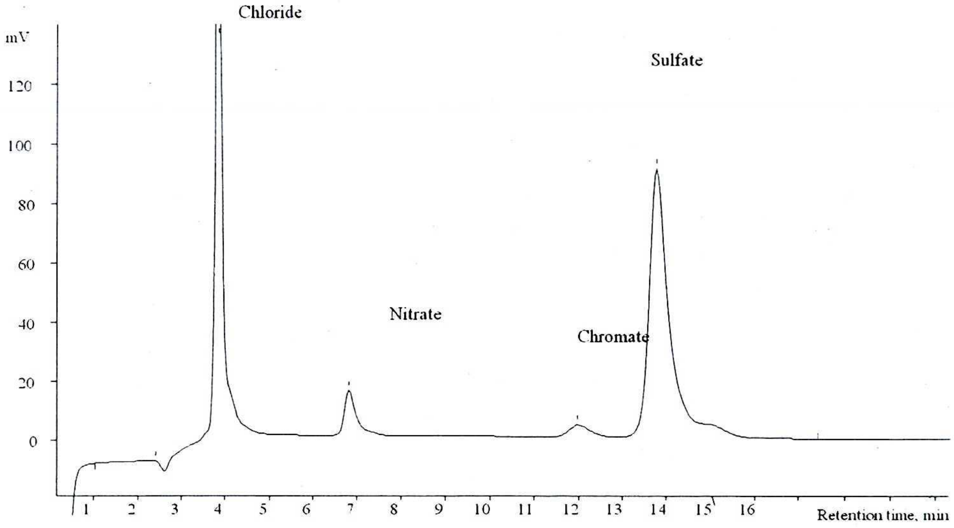

Fig. 2. Chromatogram of chromate standard (10 mg/dm^3) in tap water
Column – Dionex IonPac CS5A,
Eluent – 3.5 mM Na_2CO_3 + 1.0 mM $NaHCO_3$,
Detection – Suppressed conductivity

Calibration and method validation

Validation process was performed by testing different parameters affecting the measurements of Cr(VI) and common inorganic anions. Such parameters included method relative standard deviations, method detection and quantification limits, analysis of spiked samples, and recovery.

Ten calibration solutions of analyzed inorganic anions prepared in deonized water were injected into the eluent stream. The concentration ranges were selected according to the expected concentration of anions in the analyzed waste water.

All calibration solutions were analyzed in triplicate under optimized chromatographic conditions. Concentration ranges of analyzed anions in calibration solutions, standard deviations, accuracy, limits of detection and limits of quantification, and regression coefficients are given in Table 3.

Table 3. Method validation parameters

Parameter	Cl^-	NO_3^-	SO_4^{2-}	CrO_4^{2-}
Concentration range [mg/dm^3]	10–100	1–10	20–200	3–30
Standard deviation [mg/dm^3]	0.59	0.15	0.86	0.31
Accuracy (RSD) [%]	3.49	2.83	4.67	3.61
Limit of detection [mg/dm^3]	1.18	0.31	1.74	0.63
Limit of quantification [mg/dm^3]	3.54	0.93	3.75	1.89
Linearity (r^2)	0.9968	0.9889	0.9973	0.9891

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as six and ten times, respectively, the ratio between the standard deviation of the regression and the slope of the calibration line.

Analysis of chromate and common inorganic anions in industrial waste water

The objects of research were wastewater samples obtained in one of stainless steel plant located in Upper Silesia (Poland). After sampling, the samples were kept in dark in temperature +4°C. Because of a very high content of chloride, sulphate and heavy metals (especially chromium), this wastewater is harmful for the environment.

Total chromium content determined by ICP-MS method ranged between 2000–20 000 mg/dm^3. Moreover, the concentrations of Zn, Cd, Co, Ni, Fe and Mn were on the level of several hundred mg/dm^3. Due to this fact it was necessary to dilute samples with deonized water (1:100 v/v).

1 cm^3 of the analyzed sample was placed into 100 cm^3 calibration flask and diluted to volume with deonized water. Next, samples were filtered through a 0.15 μm membrane filter and directly injected into ion-exchange column. The results of determination of Cl^-, NO_3^-, SO_4^{2-} and CrO_4^{2-} are given in Table 4.

Table 4. Results of samples diluted with deonized water (1:100 v/v) (n = 3) [mg/dm^3]

Sample	pH	Electrical conductivity [µS/cm]	Cl^-	NO_3^-	SO_4^{2-}	CrO_4^{2-}
1	2.28	6620	87.45 ± 1.93	2.16 ± 0.11	180.42 ± 3.75	18.34 ± 0.87
2	2.14	6570	96.04 ± 2.08	1.75 ± 0.08	163.12 ± 3.12	29.67 ± 1.32
3	3.46	1090	47.11 ± 1.12	0.94 ± 0.06	101.70 ± 2.50	11.62 ± 0.41
4	2.62	5470	83.71 ± 1.74	0.71 ± 0.05	146.62 ± 2.68	22.75 ± 1.29
5	3.17	1385	30.66 ± 0.72	0.55 ± 0.04	71.08 ± 1.71	5.21 ± 0.16
6	3.09	1605	29.73 ± 0.69	0.62 ± 0.05	65.18 ± 1.42	4.87 ± 0.11
7	2.85	2950	51.94 ± 1.16	0.27 ± 0.03	44.91 ± 1.09	2.60 ± 0.08

The recovery study was performed by addition of 5.0 cm^3 of reference standard solutions (AccuIon^{TM}, NIST, USA) and 0.5 cm^3 of standard chromate solution (1 000 mg/dm^3) to wastewater sample diluted 1:100 with deonized water. The results are listed in Table 5.

Table 5. Recovery of chromate and common inorganic anions from analyzed samples

Sample	Cl^-			NO_3^-			SO_4^{2-}			CrO_4^{2-}		
	Added	Found	Recovery	Added	Found	Recovery	Added	Found	Recovery	Added	Found	Recovery
	[mg/dm^3]		[%]	[mg/dm^3]		[%]	[mg/dm^3]		[%]	[mg/dm^3]		[%]
1	1.50	1.43	95	5.00	4.38	88	7.50	7.84	104	5.00	4.68	94
2		1.60	107		4.46	89		6.92	92		4.72	94
3		1.57	105		4.52	90		6.81	91		4.60	92
4		1.42	95		5.17	103		7.70	103		4.89	98
5		1.55	103		4.62	92		6.52	87		4.75	95
6		1.63	109		4.81	96		6.69	89		4.56	91
7		1.39	93		4.40	88		7.12	95		4.37	87

CONCLUSIONS

1. Isocratic ion chromatography method using an anion-exchange column, carbonate/bicarbonate eluent and suppressed conductivity detection, applied to the determination of Cl^-, NO_3^-, SO_4^{2-} and Cr(VI) in complex matrix industrial wastewater samples is an alternative, simple, and low-cost method in comparison to wet methods used for inorganic anions analysis and hyphenated methods used for chromium determination.
2. All examined separation columns allow for simultaneous separation and determination of Cl^-, NO_3^-, SO_4^{2-} and CrO_4^{2-} ions. Simultaneous separation and determination of fluoride and phosphate eluted before chloride and sulfate is also possible in described analytical conditions. More concentrated eluent (5.0 mM Na_2CO_3 + 1.0 mM $NaHCO_3$) shortens retention times of all separated anions (Tab. 2).
3. The advantage of Dionex IonPac CS5A and AS5 columns, dedicated for the separation of highly polarizable ions, over typical anion-exchange columns is a wider pH

rage (0–14). It is important in the case of strongly acidic samples, such as analyzed metallurgical wastewater.

4. Validation parameters show good accuracy and precision, high selectivity and speed, high separation efficiency, good tolerance to complex sample matrices and very low sample pH.
5. The analyzed wastewater samples originating from metallurgy plant are characterized by high ions and metal content, and low pH values. To avoid column overloading the sample before analysis had to be diluted with deonized water.
6. Despite of sample dilution, the concentration of target anions was relatively high. The Cr(VI) content ranges from 5.21 mg/dm^3 up to 29.67 mg/dm^3. Complex sample matrix is confirmed by high electrical conductivity and low pH value even in diluted (1:100) samples (Tab. 4).
7. Chromate is highly oxidative ion and can attack some resins. Columns used in this study were able to withstand repeated (over 100 injections) high concentration of Cr(VI) as well as chloride and sulphate. Retention times, peak asymmetries and peak width for all analytes remained basically unchanged after such a long-term exposure. Similar results using gradient ion chromatography with other anion-exchange columns and eluents were described by Vanatta and Coleman [10].

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