Note

Application of ion chromatography to the analysis of chromium hydroxy salts

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(First received March 11th, 1988; revised manuscript received May 24th, 1988)

Basic (hydroxy) salts, *i.e.*, containing hydroxo groups, are widely used in industry, *e.g.*, in pigments, advanced ceramics, pharmaceuticals and tanning agents. Their exact composition, tested by quality control, is often desirable for property–structure correlations. This paper describes a general approach based on ion chromatography (IC) devoted to the complete analysis and indirect determination of the percentage basicity of similar commercial products (expressed as a percentage of equivalents of hydroxy groups present in combination with a coordinating metal). The conceptual approach is based on the overall mass balance of ionic species determined in this way in a compound or salt mixture.

This investigation relates to basic sulphatochromium salts and liquors, which are fundamental tanning media for the leather industry. Complications arising from Cr^{III} complexation by masking ligands used to regulate the tanning power, such as acetate or oxalate, make the direct injection of non-pretreated samples useless owing to the high stability of organochromium complexes. These limitations were overcome by adopting a ligand substitution technique involving 2,6-pyridinecarboxylic acid (PDCA) as powerful chelating[1–4] and releasing tridentate agent:

$$CrL_n + 2PDCA \rightleftharpoons Cr(PDCA)_2 + nL$$
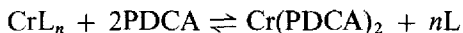
Although this pretreatment was developed specifically for use with chromium complexes, it would appear to be of general relevance and to be applicable to the IC analysis of many other strongly complexed anions.

EXPERIMENTAL

Reagents and samples

All chemicals and reagents were of analytical-reagent grade. Deionized water was used throughout.

Chromium salts masked with acetate, formate, oxalate and phthalate were prepared by mixing and boiling potassium disulphatochromate(III) [$KCr(SO_4)_2 \cdot 12H_2O$; chrome alum] with stoichiometric amounts of sodium salts of the organic acids. The molar ratios of chromium to complexing agents were 1:0.5 for monodentate and 1:0.25 for bidentate organic acids, the optimum masking effect being limited to 0.25–0.5 equiv. of the salts of the organic acid per chromium atom[5]. A mixed salt containing sodium chloride in a 1:0.5 molar ratio was also prepared in order to simulate recycled tanning liquors.

Apparatus and chromatographic conditions

A Dionex 2000i ion chromatograph equipped with a conductivity detector was used. The IC system was linked to a Shimadzu Chromatopac C-R3A digital integrator. The sample loop size was 50 μl.

The conditions for IC anion analyses were as follows: HPIC-AS4A analytical column with an HPIC-AG4A guard column and AFS-1 anion fibre suppressor (Dionex); eluent, 16 mM sodium hydrogen carbonate–18 mM sodium carbonate for general purposes and 6 mM sodium tetraborate for acetate and formate; flow-rate, 1.6 ml/min; suppressor regenerant, 0.0125 M sulphuric acid. The conditions for IC analyses of alkali metals (sodium and potassium) were as follows: HPIC-CS3 analytical column with an HPIC-CG3 guard column and a CMMS micromembrane suppressor (Dionex); eluent, 25 mM hydrochloric acid–0.25 mM 2,3-diaminopropionic acid; flow-rate, 1.0 ml/min; regenerant of CMMS, 0.1 M tetrabutylammonium hydroxide.

The ionic species investigated were identified and quantitated by comparison with mixtures of standards and by means of calibration graphs. Chromatograms obtained from typical standard mixtures of anions are presented in Fig. 1, showing the efficient separation of the six anions considered. The retention times of sodium and potassium under the above conditions were 3.1 and 4.8 min, respectively, for concentrations of 2–10 mg/l (selectivity, $\alpha = 2.03$), thus allowing a clear separation of the two very narrow peaks.

Analytical procedure

The analysis of chromium salts was carried out by dissolving 10 g of the solid in water to give 100 ml of solution (boiling for 20 min to mask) and diluting the resulting solutions to volume in water to obtain 0.15% solutions. Aliquots of 3 ml of these solutions were diluted to 50 ml and chromatographed (50-μl injections). The masked salts were pretreated by adding 30–35 ml of 0.4% PDCA solution to 3-ml aliquots and boiling under reflux for 1 h before the final dilution to 50 ml (*ca.* 0.25% PDCA, final solution concentration). Between successive injections it was essential to wait 20 min for complete elution of PDCA from the HPIC-AS4A anionic column.

Chromium when strongly complexed is not quantitatively recovered and detected by the usual IC procedures, and therefore it was determined by titrimetry. Aliquots (5 ml) of the 0.15% chromium salt solutions were first oxidized with hydrogen peroxide, then the iodine released from excess of potassium iodide was titrated with 0.05 M sodium thiosulphate standard solution. The well known high accuracy and precision of the iodimetric method (see the standard deviations in Table I) was also required in order to minimize errors in calculating the molar ratios to chromium of the analytes involved in the basicity studies.
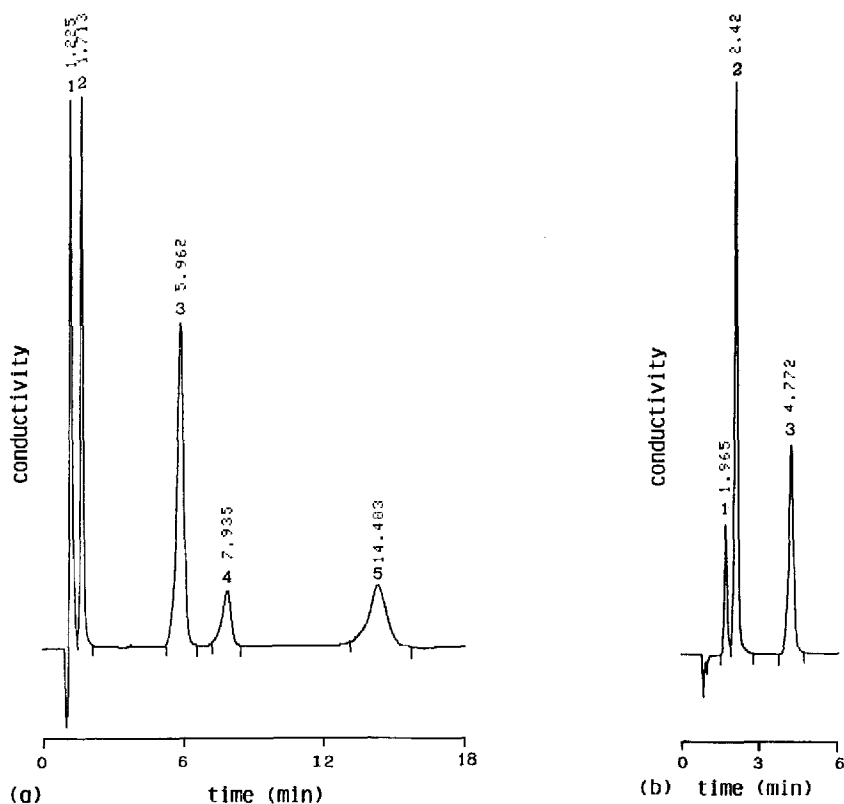
Fig. 1. Chromatograms of standard mixtures of anions. (a) Eluent, 16 mM NaHCO$_3$–18 mM Na$_2$CO$_3$. Peaks: 1 = acetate (8.0 mg/l); 2 = chloride (2.5 mg/l); 3 = sulphate (6.0 mg/l); 4 = oxalate (2.3 mg/l); 5 = phthalate (20.0 mg/l). (b) Eluent 6 mM Na$_2$B$_4$O$_7$. Peaks: 1 = acetate (6.0 mg/l); 2 = formate (8.5 mg/l); 3 = chloride (3.0 mg/l).

Basicity calculation

    The basicity of chromium salts was obtained from their percentage compositions determined by IC, *i.e.*, starting from the simplest (empirical) formulae written in terms of molar ratios n_i' and m_j' to chromium of the overall cations M$_i$ and anions L$_j$ present in the samples:

$$\sum_i (M_i)_{n_i'} Cr(OH)_x \sum_j (L_j)_{m_j'}$$

The percentage basicity (%B) related to chromium was therefore calculated from the overall mass balance of ionic species and their valencies (oxidation numbers) v_i and v_j:

$$\%B = (x/3) \cdot 100 = \left(\sum_i n_i' v_i + 3 - \sum_j m_j' v_j \right) \cdot 100/3 \tag{1}$$

TABLE I

CONCENTRATIONS OF THE IONIC SPECIES CONSTITUTING THE SYNTHETIC CHROMIUM SALTS INVESTIGATED AND PRECISION OF THE IC MEASUREMENTS

Precision expressed as relative standard deviation (R.S.D., %) of the mean value $\bar{x}$ or coefficient of variation (C.V., %); RSD = C.V. = $(S.D./\bar{x}) \cdot 100$. Results based on three determinations for each sample.

Parameter	Constituent								
	Na^+	K^+	Cr^{3+}	$HCOO^-$	CH_3COO^-	Cl^-	SO_4^{2-}	$C_2O_4^{2-}$	Phthalate
Concentration (g per 100 g)	1.0–2.1	7.1–7.4	9.5–9.8	4.2	5.4	3.3	35.4–36.3	4.1	7.6
R.S.D. (%)	2.1	1.9	1.0*	1.4	1.7	1.5	1.6	1.7	2.3

* Titrimetric (iodimetric).

The influence of the experimental errors of the individual determinations on the precision of the final result, *i.e.*, the absolute uncertainty in the calculated value of %*B*, was calculated using propagation errors theory[6]. The standard deviations (S.D.) of the molar ratios in eqn. 1 were calculated from the S.D. of the molar composition of each ionic species and of the chromium.

RESULTS AND DISCUSSION

Table I gives typical analytes that constitute basic chromium salts or liquors, their concentrations in the investigated synthetic samples and the precision of the IC measurements (chromium was determined by oxidimetry).

Sodium, potassium, formate, acetate and chlorine were quantitatively evaluated using the heights of their narrow peaks and sulphate, oxalate and phthalate using the areas of their broader peaks. The average precision of the PDCA pretreatment and of the chromatographic procedure as indicated by the reported relative standard deviations (R.S.D.), was found to be *ca*. 2%, ranging from 1.4% (formate) to 2.3% (phthalate). The reproducibility obtained seems satisfactory and might be due to the high quality of the pump delivery system.

The recovery of the masking ligands released by the PDCA pretreatment was also found to be almost complete (Table II). The relative errors of the compositions found ranged from 1.5% for formate to 2.4% for oxalate, showing the good accuracy of the PDCA pretreatment. The results obtained therefore demonstrate the reliability of the IC method and of the proposed sample pretreatment in the analysis of ionic species in basic sulphatochromium compounds.

The amounts of PDCA and the pretreatment (boiling) time were previously assessed by performing recovery studies based on stressed limiting conditions, *i.e.*, using as a reference masked salt the very stable chromium(III)–oxalate 1:2 complex (with the strongest chelating effect of the masking ligands considered). The high molar ratio of complexation in the standard complex (1:2) exceeded 10-fold the common values of commercial oxalate-masked salts (1:0.25), thus ensuring the effectiveness of the pretreatment parameters optimized with respect to routine analyses with wide confidence margins.

Fig. 2 shows the results of the investigation to establish the optimum complexation conditions of the Cr^{III} reference salt with PDCA which accounts for both the amount (0.25%, final solution concentration) and the time (1 h) recommended for

TABLE II

ACCURACY OF THE PDCA PRETREATMENT FOR THE SYNTHETIC CHROMIUM SALTS INVESTIGATED

Masking ligand	Expected (g per 100 g)	Found ± S.D. (g per 100 g)	Recovery (%)	Relative error (%)
$HCOO^-$	4.15	4.09 ± 0.06	98.5	1.5
CH_3COO^-	5.46	5.36 ± 0.09	98.0	2.0
$C_2O_4^{2-}$	4.13	4.03 ± 0.07	97.6	2.4
Phthalate	7.56	7.40 ± 0.17	97.9	2.1

TABLE III

COMPOSITION AND PERCENTAGE BASICITY CALCULATIONS WITH PRECISION AND ACCURACY

Sample	Constituents	Molar ratio	Expected		Found*			%B (% basicity units)			
			g per 100 g	mol/kg	g per 100 g	mol/kg	S.D. (mol/kg)**	Ex-pected	Found	S.D.***	Absolute error
Chrome alum	K⁺	1	7.83	2.002	8.0	2.05	0.04				
	Cr³⁺	1	10.41	2.002	10.4	2.00	0.02				
	SO₄²⁻	2	38.48	4.004	39.0	4.06	0.06				
	KCr(SO₄)₂ · 12H₂O							0.0	−1.2	2.2	1.2
33% basic sulphate	Na⁺	1	7.86	3.421	7.4	3.21	0.07				
	K⁺	–	–	–	0.66	0.17	0.004				
	Cr³⁺	1	17.79	3.421	17.5	3.36	0.04				
	SO₄²⁻	1.5	49.29	5.131	48.6	5.06	0.08				
	(Na,K)CrOH(SO₄)₃/₂							33.3	32.7	2.1	0.6
Masked 33% basic sulphate	Na⁺	1.5	10.58	4.602	10.3	4.48	0.08				
	K⁺	–	–	–	0.61	0.15	0.003				
	Cr³⁺	1	15.96	3.069	16.2	3.12	0.03				
	SO₄²⁻	1.5	44.22	4.602	44.8	4.66	0.07				
	C₂O₄²⁻	0.25	6.76	0.767	6.6	0.75	0.01				
	(Na,K)CrOH(SO₄)₃/₂ · ¼Na₂C₂O₄							33.3	34.3	2.3	1.0

* Results based on three determinations for each sample.

** S.D. of the molar ratio of the species i (or j) was calculated from these values by means of the equation $s'_i = (n_i/n_{Cr})[(s_i/n_i)^2 + (s_{Cr}/n_{Cr})^2]^{1/2}$, where s'_i = S.D. of the molar composition n_i of the species i (or j) and s_{Cr} = S.D. of the molar composition n_{Cr} of the chromium.

*** S.D. of $\%B = s_B = \left[\sum_i (s'_i)^2 + \sum_j (s'_j)^2\right]^{1/2} \cdot 100/3$, where s'_i and s'_j are the S.D.s of the molar ratios of species i and j.
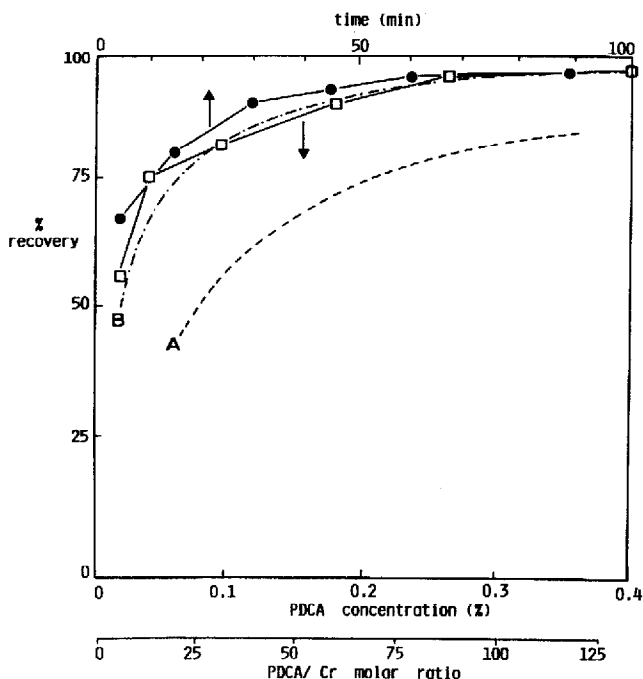
Fig. 2. Effect of the amount of PDCA and pretreatment (boiling) time on the recovery of oxalate from the Cr–oxalate 1:2 complex. Lower scale, boiling time fixed at 1 h; upper scale, amount of PDCA fixed at 0.25% (final solution concentration). A and B are recoveries provided by eqn. 3 with different hypothesis, B taking into account the influence of pH.

completing the masking ligand substitution with PDCA. Under the reaction conditions used (boiling for 1 h), the oxalate recovery was about 50% for PDCA:Cr molar ratios of the same order of magnitude as the stoichiometric ratio required for chelation (2:1), approaching a limiting value of 97.5% when the molar ratios were increased to 50–60 times the initial values. Hence from a practical point of view a large excess of PDCA is necessary to complete the substitution of the oxalate chelating ligand as rapidly as possible.

Completeness of the ligand substitution reactions is regulated by both thermodynamic (*i.e.*, ratios of the respctive conditional formation constants) and kinetic factors, the ligand exchange kinetics of Cr^{III} being very slow. The effect of the kinetic factors is illustrated in the top experimental graph in Fig. 2, showing that equilibrium conditions are reached after boiling for *ca.* 1 h.

Thermodynamic factors require much more discussion. In this respect it is useful to compare the experimental recovery curve (at constant time) shown in the Fig. 2 with the theoretical plots obtained by equilibrium calculations. When two ligands are present, which complex is formed depends on the ratio of the overall equilibrium constats and the ratio of the ligand concentrations. For the system Cr–oxalate–PDCA the equilibrium constant K of the reaction

$$Cr(Ox)_2^- + 2PDCA^{2-} \rightleftharpoons Cr(PDCA)_2^- + 2Ox^{2-} \qquad (2)$$
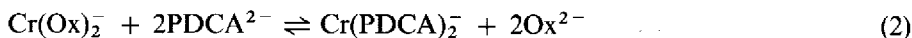
is $K = {}_{PDCA}\beta_2/{}_{Ox}\beta_2 = 4.36 \cdot 10^7/3.23 \cdot 10^{10} = 1.35 \cdot 10^{-3}$, ${}_{Ox}\beta_2$ and ${}_{PDCA}\beta_2$ being the overall formation constants of the oxalate[7] and the PDCA[1] 1:2 complexes, respectively $({}_{Ox}\beta_2 = {}_{Ox}K_1 \cdot {}_{Ox}K_2 = 2.18 \cdot 10^5 \cdot 1.48 \cdot 10^5)$. Thus the [PDCA^{2-}] equilibrium concentration will be

$$[\text{PDCA}^{2-}] = \left[\frac{c\alpha(c2\alpha)^2}{Kc(1 - \alpha)}\right]^{1/2} \tag{3}$$

$$= c' - c2\alpha \approx c'$$

where c is the initial molar concentration of chromium, c' is the total concentration of PDCA^{2-} (free and combined) and α is the recovery. Substituting in eqn. 3 the experimental value of c ($1.8 \cdot 10^{-4}$ mol/l), one can obtain the plot of $\alpha\%$ *versus* [PDCA^{2-}] or PDCA% (dashed line in Fig. 2). The theoretical results so obtained appear to be inconsistent with the experimental results (bottom experimental graph in Fig. 2). A much better theoretical model can be obtained by taking in account that the oxalate ligand is derived from a weak acid, *i.e.*, the species Ox^{2-} is subtracted from the complexation equilibrium by the hydrolysis reaction. Therefore, making use of the dissociation constants of oxalic acid ($pK_{a_1} = 1.25$, $pK_{a_2} = 4.28$) we obtain the following generalized form of the ${}_{Ox}K_1'$ conditional formation constant, showing pH dependence[8]: ${}_{Ox}K_1' = {}_{Ox}K_1/(1 + [\text{H}^+]K_{a_2} + [\text{H}^+]^2K_{a_1} \cdot K_{a_2})$.

Our recovery experiments were carried out at pH 3.5 in order to give a maximum yield of the Cr(PDCA)$_2^-$ complex[1]. At pH 3.5, ${}_{Ox}K_1' = 3.09 \cdot 10^4$. From this value one can calculate the value of the effective or conditional constant of eqn. 2 at the considered pH: $K' = {}_{PDCA}\beta_2/{}_{Ox}\beta_2' = {}_{PDCA}\beta_2/{}_{Ox}K_1' \cdot {}_{Ox}K_2 = 9.54 \cdot 10^{-3}$. Substitution of this K' value in eqn. 3 allows a new plot of $\alpha\%$ *versus* [PDCA$^-$] and also PDCA% to be drawn (dotted and dashed line in Fig. 2), which agrees very satisfactorily with the experimental trend. The high yields of the oxalate recovery shown in Fig. 2 account for the good recoveries of the other masking ligands (Table II) whose formation constants are 100 times lower (the pK_1 values of the first formation constants of the Cr–formate and the Cr–acetate complexes are *ca.* 3).

From the R.S.D. values in Table I it would possible to calculate the S.D.s of the molar ratios of the analytes that constitute typical basic salt formulations of approximately known composition. Therefore, this would allow to the precision to be obtained when calculating their basicity from eqn. 1. At compositions of the same order of magnitude as those shown in Table I, a precision of *ca.* 2% basicity units was obtained for oxy salts composed of three or four ionic species (Na$^+$ or K$^+$, Cr^{3+}, SO$_4^{2-}$ and masking anion).

Table III summarizes the experimental data for chrome alum, 33% basic sodium sulphate (commercial grade, 26% Cr$_2$O$_3$) and the same 33% basic salt masked with sodium oxalate with a Cr:C$_2$O$_4^{2-}$ molar ratio of 1:0.25. The S.D. values of the percentage basicity range from 2.1 to 2.3 percentage basicity units and the absolute errors range from 0.6 to 1.2 percentage basicity units. In the samples examined basicity can therefore be determined with satisfactory precision and accuracy for composition quality control. In contrast, the classical alkalimetric methods give large errors in the presence of masking agents.

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