

Estimation of trace quantities of chromium using coprecipitation properties of lanthanum hydroxide

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Coprecipitation properties of lanthanum hydroxide precipitate has been used for preconcentration of water samples, containing trace quantities ($\mu\text{g dm}^{-3}$) of $\text{Cr}^{\text{VI}}/\text{Cr}^{\text{III}}$. The precipitate is able to carry, quantitatively both forms of Cr at $[\text{La}^{\text{III}}] > 100 \text{ mg dm}^{-3}$ at $\text{pH} > 7$ and can be effectively used for trace analysis of Cr.

The acute toxicity of chromium in hexavalent state has led to the development of various analytical techniques for its estimation in trace quantities^{1,2}. In spite of very low detection limit ($0.05\text{-}1.5 \mu\text{g dm}^{-3}$) of some methods, preconcentration of samples is often required. The tendency of Cr to quantitatively coprecipitate *in situ*, with series of precipitates can be used for preconcentration of water samples³⁻⁵. Iron(III) hydroxide and aluminium hydroxide have been widely used in this regard. However, the concentration range and other conditions, most favourable for an effective preconcentration are still obscure for many precipitates. In this study *in situ* coprecipitation of Cr, with $\text{La}(\text{OH})_3$ precipitate, was studied under different conditions, from water samples containing $0.01\text{-}1.0 \text{ mg dm}^{-3}$ of chromium. The extent of binding of Cr with $\text{La}(\text{OH})_3$ precipitate, followed by its recovery in residue, was determined by Flame Atomic Absorption Spectrometry and by tracer technique using ^{51}Cr isotope. The same preconcentration method was used to determine total Cr in some ground water samples.

Experimental

Potassium dichromate and lanthanum chloride used for preparing stock solutions of Cr^{VI} and La^{III} were of A R grade and ^{51}Cr was received from BRIT, BARC, India. The preparation of samples and preconcentration was achieved by adopting the following procedure.

In the water samples 250 cm^3 , $[\text{Cr}^{\text{VI}}] = 0.1 \text{ mg}$

dm^{-3}), prepared by diluting stock solution of Cr^{VI} using preacidified ($\text{pH} = 3.5$) water, different doses of La^{III} (Table 1A) were added. Sodium sulphite solution was used to reduce Cr^{VI} in order to generate samples of Cr^{III} . The precipitation of La^{III} , alongwith coprecipitation of $\text{Cr}^{\text{III}}/\text{Cr}^{\text{VI}}$ was achieved by adding calculated (necessary to generate the required pH) volumes of NaOH ($6N$). After centrifuging at 3200 rpm, the residue, thus obtained, was dissolved in 25 cm^3 (final volume) of HCl ($\text{pH} = 2$). The chromium concentration was determined in this solution by employing Perkin Elmer 2380 Flame Atomic Absorption Spectrometer (FAAS). While using tracer technique, 1 cm^3 of ^{51}Cr (equivalent to $3 \mu\text{Ci}$) solution, in respective oxidation state, was added before precipitation and 5 cm^3 of the final solution was counted in a standard geometry over $\text{NaI}(\text{TL})$ gamma ray detector, coupled with 4k multichannel analyser. Double distilled deionized water was used through out the experiments carried out in triplicate. The results were reproducible within $\pm 4\%$ deviation.

Results and discussion

The mean values of results, obtained for each set of experiments, are presented in Table 1. The excess of La^{III} do not interfere in FAAS measurements, but at $[\text{La}^{\text{III}}] < 100 \text{ mg dm}^{-3}$, preconcentration of samples is not quantitative with respect to chromium. Hence, further experiments were conducted only at $[\text{La}^{\text{III}}] = 100 \text{ mg dm}^{-3}$, which is the minimum concentration of La^{III} able to quantitatively carry Cr from water samples, with initial concentrations of Cr ranging from $0.01\text{-}1.00 \text{ mg dm}^{-3}$ (Table 1B). The variation in pH has also a marked effect and effective preconcentration is possible only at $\text{pH} > 7$ (Table 1C). In case of Cr^{VI} , the effect of pH might be associated with the equilibrium between CrO_4^{2-} and HCrO_4^- . At $\text{pH} > 7$, CrO_4^{2-} is the major species which is largely coprecipitated. Regarding Cr^{III} , it is known⁴ that it exists at acidic pH as the hexa-aqua ion $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, which has pK of 4. At slightly higher pH the hydroxide ion $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ is formed which can give soluble dimers and polymers. At still higher pH , dark green gels are formed, which are coprecipitated with $\text{La}(\text{OH})_3$. Coprecipitation of an ion by a precipitate is generally, accompanied by its adsorption followed by incorporation into precipitate matrix. Therefore, net carrying over of the trace

Table 1—Mean values of % recovery of chromium, after ten fold preconcentration of sample at pH 9 (unless defined) under varying [Cr^{III/VI}]/[La^{III}] ratios

	[Cr ^{III/VI}] mg dm ⁻³	[La ^{III}] g dm ⁻³	% recovery			
			Cr ^{VI}		Cr ^{III}	
			*	**	*	**
A	0.10	0.50	97.3	100.4	97.0	99.2
	0.10	0.30	95.0	97.4	95.8	96.2
	0.10	0.20	94.6	96.3	96.0	96.0
	0.10	0.10	93.5	94.0	95.4	96.3
	0.10	0.06	72.2	76.9	60.3	65.9
	0.10	0.02	41.5	40.2	35.1	37.3
B	1.00	0.10	98.2	101.8	96.3	100.4
	0.50	0.10	97.6	97.0	96.4	98.0
	0.20	0.10	96.2	100.2	95.1	96.8
	0.10	0.10	93.5	94.0	95.4	96.3
	0.01	0.10	95.1	94.3	95.0	94.5
C	0.01(a)	0.10	8.8	12.6	11.3	14.7
	0.01(b)	0.10	69.2	70.2	67.4	64.0
	0.01(c)	0.10	84.0	85.8	87.2	88.1
	0.01(d)	0.10	96.2	97.0	97.5	97.0
	0.01(e)	0.10	98.4	101.0	100.6	101.2

Measurements from (*) FAAs, (**) Gamma Spectrometer
pH values; (a) = 4, (b) = 5, (c) = 6, (d) = 7, (e) = 10.

Table 2—Average data for total dissolved chromium in ground water, as determined by ten fold preconcentration, at pH 9, followed by FAAS measurements

Sample No.	Horizontal distance from effluent drain/km	[Cr]/ $\mu\text{g dm}^{-3}$
1	1.5×10^{-2}	9.2
2	2.0×10^{-2}	9.9
3	0.1	11.8
4	0.2	23.1
5	0.8	47.1
6	1.0	42.4
7	2.5	9.6
8	4.0	ND
9	5.0	ND

ND: Not detectable

50-65 m) around an open, uncemented drain, carrying mixed effluent from a cluster of tanneries (operating since last 30-40 years) (Table 2), to its final discharge point, Yamuna river. Though, the Cr concentration in ground water is below permissible limit ($50 \mu\text{g dm}^{-3}$), yet horizontal and vertical mobility of Cr, through soils layers, is evident, which is most likely through the formation of organo-chromium complexes.

References

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ion depends upon various complex parameters. In spite of poorly defined nature of most of these parameters, in case of La(OH)₃ precipitate, including uncertainty about its stoichiometry, it effectively carries Cr from aqueous solutions.

The applicability of this method in real samples was checked by applying it to determine total dissolved Cr in ground water (samples collected from a depth of