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Micro Analysis of Selected Transition Metals Using Carrier Precipitation and Speciation of Chromium

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A study was undertaken for successive analysis of micro amounts of transition metals in aqueous samples. Amongst the four carriers examined, $Y(OH)_3$ has been found to be an efficient carrier for quantitative separation and preconcentration of elements in µg and sub µg range. The analytical scheme is simple to adapt and requires minimal experimental set up. In addition, Cr(III) and Cr(VI) in aqueous samples can be determined through direct carrier precipitation and reductive coprecipitation with the carrier ions.

INTRODUCTION

Determination of elements of interest in µg or sub µg range is of particular importance in several fields of science and technology. Amongst others in medicine, criminology, food science, environmental determinations, semiconductor and metallurgical industry there is persistent demand for analytical methodology for the quantification of trance elements. Their minute concentrations can dramatically alter the metabolic behavior of living tissues or chemical and physical properties of a product fabricated industrially. Analytical quantification at trace level is often realized with improved selectivity and sensibility by preconcentration or enrichment of analyte entailing elimination of undesirable matrice material before analytical determination.

Popular preconcentration techniques developed incorporate carrier precipitation, solvent extraction, ion exchange separation, or analyte sorption on solid surfaces[1–7]. Suitability of a preconcentration step is generally governed by the nature of the sample and the analytical technique employed for data collection. However, it remains that for routine analysis the analytical scheme should be easily adaptable, inexpensive and effective. In this context carrier precipitation of trace elements using selective inorganic and organic collectors has been well exploited[8]. Several literature studies reveal multiple use of hydroxides of iron[9, 10], aluminium[11, 12], lanthanum[13–15], manganese[16] and zirconium[17, 18] as efficient collectors for the recovery of a host of trace metals from a variety of samples of industrial and environmental importance. More recent studies describe the use of scandium[19], hafnium[20] and gallium[21] hydroxides for trace elements collection from aqueous samples.

The present communication comprises a study of the efficacy of relatively unexplored yttrium hydroxide as collector for micro amounts of selected metals in aqueous and solid samples. In addition this approach has been coupled with an induced reductive reaction for the speciation of Cr(III) and Cr(VI) in an aqueous system.

EXPERIMENTAL

Stock solutions of metal ions at 1000 ppm were prepared by dissolving their chloride or nitrate salts of analytical grade quality or superior in deionized distilled water. Yttrium nitrate at 5% concentration was prepared by dissolving 5 g of salt in 100 mL deionized distilled water. Sodium arsenite was employed as solid reductor. A 4 M solution of NaOH was utilized for precipitation of $Y(NO_3)_3$ in a sample solution. Metal ion concentration in each case was determined in flame atomic absorption mode with Perkin-Elmer-5000 atomic absorption spectrophotometer fitted with deuterium background correction.

Preconcentration procedure

To 500 mL of water solution metal ions were spiked to obtain concentrations ranging from 0.4 to 0.06 ppm in the final volume. Each concentration was examined in quadruplet. the metal ions were coprecipitated in each case by addition of 2 mL of 5% $Y(NO_3)_3$ followed by 2–3 mL of 4 M NaOH. The precipitation was affected slowly under constant stirring and the precipitated material was set aside for equilibration for about 3 h. The $Y(OH)_3$ precipitate was millipore membrane filtered (0.45 μM pore size) under suction and washed twice with 10 mL deionized water. The membrane thereafter was placed in 150 mL clean beaker and the precipitate dissolved in 10 mL of 2 M HCl. The solution was quantitatively transferred into 25 mL standard flask. Metal ion concentration was determined in each sample by atomic absorption spectrophotometer in flame mode. The chemical yield was obtained by comparison with metal ion standards also mixed with 2 mL of $Y(NO_3)_3$ to match the matrix.

For speciation of Cr(III) and Cr(VI), the procedure entailed precipitation separation of Cr(III) in an aliquot (up to 100 mL) under the conditions described for general coprecipitation, while in another equivalent aliquot Cr(VI) was brought to Cr(III) state by addition of 300 mg solid sodium arsenite as reductor and boiling the solution for about 10 min. Total chromium as Cr(III) was determined thereafter by carrier precipitation as above. Cr(VI) could be obtained by difference from the total by subtracting Cr(III)·determined earlier.

For solid samples (*e.g.*, soils) the experimental approach incorporated metal ion extraction from the matrix by dissolution. the weighed sample (*ca.* 0.5 g) was treated with 10 mL 8 M HNO_3 followed by addition of 5 mL H_2O_2 (30%) and the extraction realized by maintaining the solution close to boiling for about 30 min. The sample volume was brought to 25 mL by filtration and metal ions concentrations determined by carrier precipitation as described above.

RESULTS AND DISCUSSION

In the initial phase optimum carrier ion concentration was determined by examining recoveries of 4 and 2 ppm solutions of two or three test metals by varying $Y(NO_3)_3$ concentration from 50 to 300 mg. The data showed that 100 mg $Y(NO_3)_3$ was adequate (*ca.* 98% recovery) for up to 500 mL sample volume and hence this was maintained throughout this study. Based on this observation several studies were conducted to ascertain recovery of some selected transition metals in μg range. The results (Table-1) show that up to 0.06 ppm (60 ng/mL) metal recovery in most cases is realizable satisfactorily. The relative standard deviation of mean values in most cases centred around 5–6% at the most.

TABLE-1
RECOVERY (%) OF METALS VIA CARRIER PRECIPITATION WITH $Y(NO_3)_3$ 100 mg

Conc. (ppm)	Zn	Cd	Pb	Mn	Cu	Ni	Cr	Fe	CO	Rh	Pd	In
0.40	95.5	95.2	94.70	87.2	99.12	91.5	88.90	90.28	89.2	N.D.	N.D.	94.50
0.20	96.9	94.7	96.20	90.3	98.60	91.4	87.30	90.07	81.2	N.D.	96.0	95.05
0.10	98.7	92.8	101.08	89.6	94.25	96.1	78.36	92.14	S.L.R.	95.8	93.6	101.42
0.06	86.9	91.8	96.00	S.L.R.	S.L.R.	S.L.R.	S.L.R.	S.L.R.	S.L.R.	96.8	96.4	95.30

N.D.: Not determined; S.L.R.: Significantly lower recovery

The procedure described was applied toward analysis of metals in soil samples. A standard soil sample (CCRM # soil SO-1) was analyzed by this procedure for some metals known to be present in this matrix. The experimental data show that reasonable recoveries of trace metals can be realized as shown in Table-2.

TABLE-2
RECOVERY OF SOME TRACE METALS FROM SOIL SAMPLE (CCRM # SOIL SO-1)

Conc. (< g/g)	Cr	Zn	Ni	Cu
Expected	160.00	146.00	94.00	61.00
Found	156.12	134.05	100.48	58.45
% Recovery	97.57	91.81	106.89	95.82

The speciation of Cr(III) and Cr(VI) has been a subject of interest, since two oxidation states of the element chromium exhibit different characteristics. In Cr(III) state it is an essential nutrient element as required for lipid and glucose metabolism in mammals, while in Cr(VI) state it has carcinogenic and toxic properties towards living organisms[22, 23]. Determinations of Cr(III) and Cr(VI) have been described in several studies of clinical and biological importance[22–25] and analytical and environmental interest[20, 24, 26–28]. In this study speciation of Cr was attempted by a double analysis. In the first instant in an aqueous sample of Cr(III) and Cr(VI), the former was carrier precipitated as usual with $Y(OH)_3$ and determined by atomic absorption spectrophotometer. For Cr(VI) which escapes carrier precipitation an induced reductive reaction was incorporated that could convert Cr(VI) to Cr(III). This conversion of chromium in Cr(III) state permits total chromium determination by carrier precipitation as described earlier from which Cr(VI) can be calculated.

Amongst the several reductors examined for Cr(VI) conversion to Cr(III) which included ferrous ammonium sulphate and ascorbic acid, the best results were obtained with $NaAsO_2$. The arsenite reduction in fact occurs at an elevated temperature and the reduction proceeds in steps as shown below[29]

$$\begin{aligned} \mathrm{Cr(VI)} + \mathrm{As(III)} &\rightarrow \mathrm{Cr(IV)} + \mathrm{As(V)} \\ \mathrm{Cr(IV)} + \mathrm{Cr(VI)} &\rightarrow 2\mathrm{Cr(V)} \\ \mathrm{Cr(V)} + 2\mathrm{As(III)} &\rightarrow \mathrm{Cr(III)} + 2\mathrm{As(V)} \end{aligned}$$

$$2\mathrm{Cr(VI)} + 3\mathrm{As(III)} \rightarrow 2\mathrm{Cr(III)} + 3\mathrm{As(V)}$$

Optimum arsenite concentrations for 100 mL Cr(VI) solutions of 4 and 2 ppm were experimentally determined by addition of solid sodium arsenite varying from 50–750 mg. Interestingly constant results were obtained in 100–300 mg $NaAsO_2$ range (recovery > 98%), while above and below this range there was significant decrease for Cr recovery. Hence 300 mg $NaAsO_2$ was employed as optimum reductor concentration. The analytical data show that up to 0.26 ppm of chromium can be quantified successfully directly by flame atomic absorption spectrophotometer in aqueous samples without carrier preconcentration. Hence in any analytical scheme the Cr concentration should remain superior to this threshold concentration for meaningful results.

The efficacy of this approach was further ascertained by successive analysis of Cr(III) and Cr(VI) in the same solution at various concentrations of the two species. Data in Table-3 show that recovery of Cr(III) alone and that of total chromium [Cr(III) + Cr(VI)] remains quantitative. These data are supportive of Cr speciation in μg range though in principle it should remain feasible in sub μg range as well provided the total chromium concentration remains superior to instrumental operational detection limit which centers around 0.26 ppm in direct flame atomic absorption spectrophotometric analysis as described earlier.

TABLE-3
SPECIATION OF Cr(III) AND Cr(VI) BY DIRECT AND REDUCTIVE CARRIER PRECIPITATION WITH $Y(NO_3)_3$

Volume 40 mL, $Y(NO_3)$ 100 mg, $NaAsO_2$ 300 mg

Mixture proportions (μg/40 mL)		*Cr(III)%	†Cr (Total) %
Cr(III)	Cr(VI)		
10.4	5.2	99.5	98.7
10.4	2.08	101.0	94.95
5.2	1.04	99.8	96.00

*Mean value (n = 4) for carrier precipitation without sodium arsenite representing Cr(III) recovery.

†Mean value (n = 4) for carrier precipitation with sodium arsenite representing total Cr recovery.

The present study with $Y(OH)_3$ as carrier for trace element depicts some superiority over the other metal hydroxides in selective cases. A comparative study for Cr(III) (4 ppm) coprecipitation with In, Al, Fe and Y hydroxides showed that percentage recoveries occur at 43.2, 115.4, 96.3 and 98.3 respectively. Low results with In and high results with Al present somewhat inefficient behavior of these carriers, while recoveries with Fe and Y are parallel. However, yttrium remains preferable since Fe stock solution can only be preserved in very highly acidic medium to prevent its hydrolytic precipitation, while for Y no hydrolytic precipitation is observed even when its solution is maintained in mildly acidic medium. Hence $Y(OH)_3$ carrier precipitation for micro and trace elements analysis in appropriate samples can be recommended and this simple procedure can be applied for trace elements determination in natural waters, soils and appropriate industrial fabrications.

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