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Use of Carrier Technique for Preconcentration of Microamounts of Cr(VI): A Radioindicator Study

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Abstract

Based on a scientific study of the deposition of radioactive $^{51}CrO_4^{2-}$ species on ignited microcrystalline sulfates of lead, barium, and strontium along with their subsequent elution, a new experimental procedure for the concentration of aqueous extracts of microgram quantities of chromate species is developed. The feasibility of the procedure has been studied radiometrically on the basis of a systematic examination of the working conditions, e.g., carrying efficiency as a function of pH of the aqueous medium lattice/nonlattice ionic concentration, amount of carrier, carrying capacity of the carrier, and extraction of activity adsorbed under suitable experimental conditions. In principle, the procedure consists of two stages: first, the radioactive tracer species in a dilute aqueous solution is carried out under specified experimental conditions on a small quantity of ignited selected carriers; second, the carried activity can be largely leached out in a minimal amount of water of specified activity.

INTRODUCTION

Chromium compounds, especially those of chromium(VI), are toxic. In view of the large number of important applications of chromium compounds in industrial operations, e.g., leather, textile, and metal finishing, the industrial discharge of chromium-bearing wastes has created environmental problems.

Various sorption methods have been used for the removal of Cr(VI)

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from waste solutions, including the adsorption colloid flotation method (*1*) and the reduction-coprecipitation technique (*2*). Studies on the removal of Cr(VI) from aqueous solution with different carriers, e.g., metal iodates (*3*), sulfates (*4*), carbon black (*5*), and fly ash–wollastonite (*6*), have also been reported. In fact, the removal of ions from solutions and their determination by concentration of several trace materials by adsorption on different sulfate and oxide carriers has attracted increasing attention of a

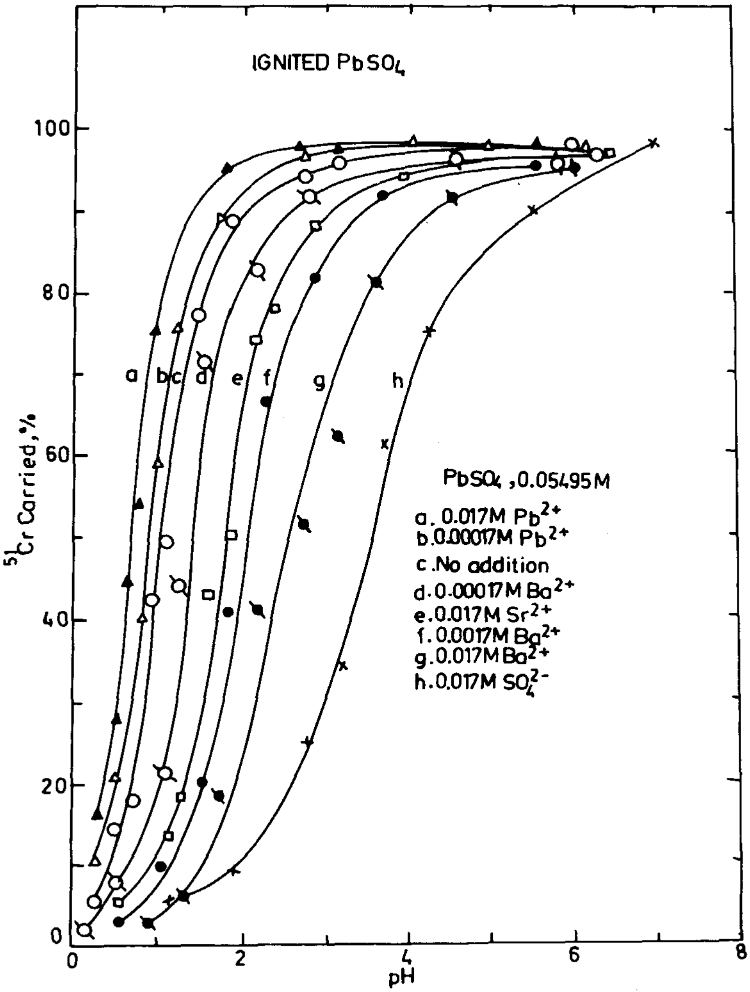

FIG. 1. Carrying vs pH.

large number of workers (*7*, *8*) because it offers a useful alternative for rapid separations (*9*). Our findings, based on deposition of the $^{51}CrO_4^{2-}$ species, illustrate the possibility of the removal and separation of radioactive tracers by using lead sulfate, barium sulfate, and strontium sulfate as carriers (*10*). This possibility is based on the fact that adsorption of the tracer is complete at widely different pH values. Moreover, the same ad-

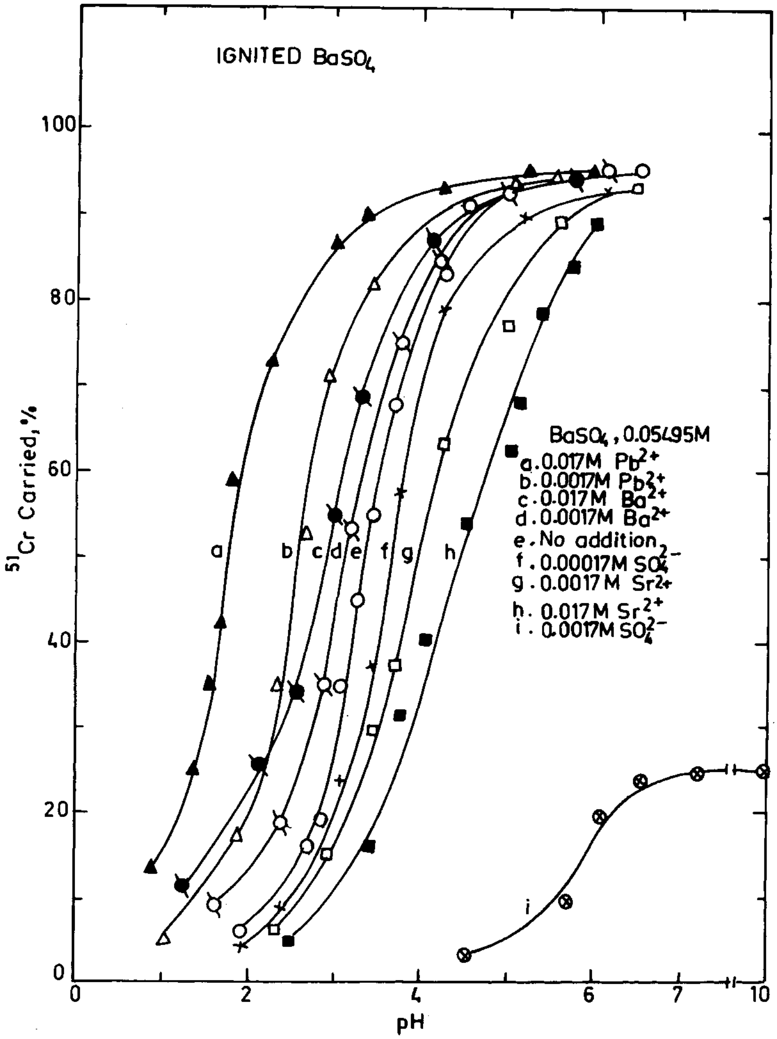

FIG. 2. Carrying vs pH.

sorbent found efficient for one tracer does not carry the activity of the other tracers under the same set of experimental conditions. Examples are the carrying of $^{51}CrO_4^{2-}$ ions on ignited strontium sulfate (Fig. 3) and on $^{32}PO_4^{3-}$ species (*11*). Hence, a clear-cut retention of >95% or <5% activity can be achieved. However, the disadvantage of the method, recognized and reported by Girardi et al. (*12*), is that data obtained from experiments with single components may not apply exactly to samples containing other substances.

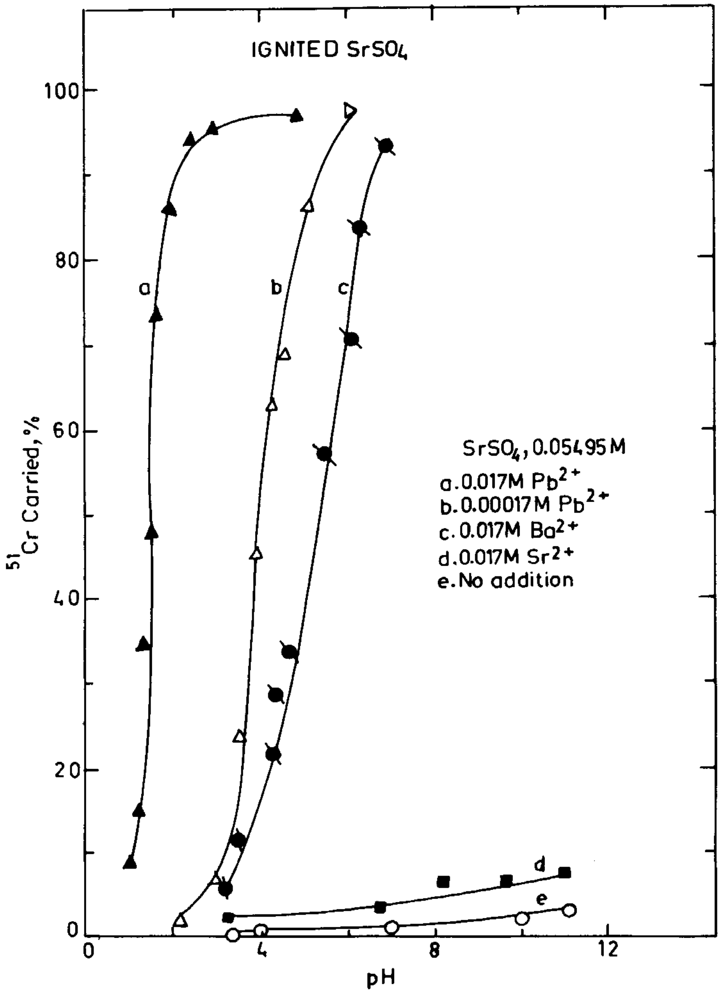

FIG. 3. Carrying vs pH.

Concentration procedures for $^{32}PO_4^{3-}$ and $^{76}AsO_4^{3-}$ ions using ignited barium sulfate as the carrier were reported by Kar and coworkers (*13*, *14*). In this context, our findings on the carrying of CrO_4^{2-} tracer as reported in Figs. 1–3 look significant. It has been shown that under specified experimental conditions, chromium ions present as the chromate species in aqueous solution at tracer concentration are carried instantaneously and almost completely by small quantities of these preformed ignited ionic compounds. Further, preliminary experiments show that the activity carried under the specified conditions can be recovered more or less quantitatively by leaching the carrier with acidified water.

On the basis of the above observations, it may be possible to develop a new experimental procedure for concentrating the aqueous extracts of chromate tracer. In the present investigation the feasibility of the procedure is studied by a systematic examination of the working conditions.

EXPERIMENTAL

Materials and Methods

Ignited samples of lead sulfate, barium sulfate, and strontium sulfate were prepared according to a standard procedure (*15*). Cr-51 in the form of sodium chromate in an isotonic saline solution (specific activity 15 mCi/mg of Cr) was procured from B.A.R.C., Trombay. Our experimental procedure for estimating the radioactivity was exactly the same as that reported earlier (*3*). A single channel gamma-ray spectrometer (GRS-23) coupled with a 2″ × 2″ NaI(Tl) well-type detector was used for assaying the gamma activity. All experiments were done in a total volume of 12 mL.

Procedure

In principle, the procedure consists of two stages: first, the radioactive tracer in a dilute aqueous solution is carried under specified conditions on a small quantity of ignited selected carriers; second, the carried activity after washing can be largely leached out in a minimal amount of water of specified acidity. Like other extraction processes, 3–4 extractions are needed for the maximum recovery of radioactivity.

RESULTS AND DISCUSSION

The results are presented in Figs. 1–4 and Tables 1–4. The instantaneous carrying of radioactive tracer on ignited carriers has been shown to be due to surface adsorption. Further, the process has been found to be highly

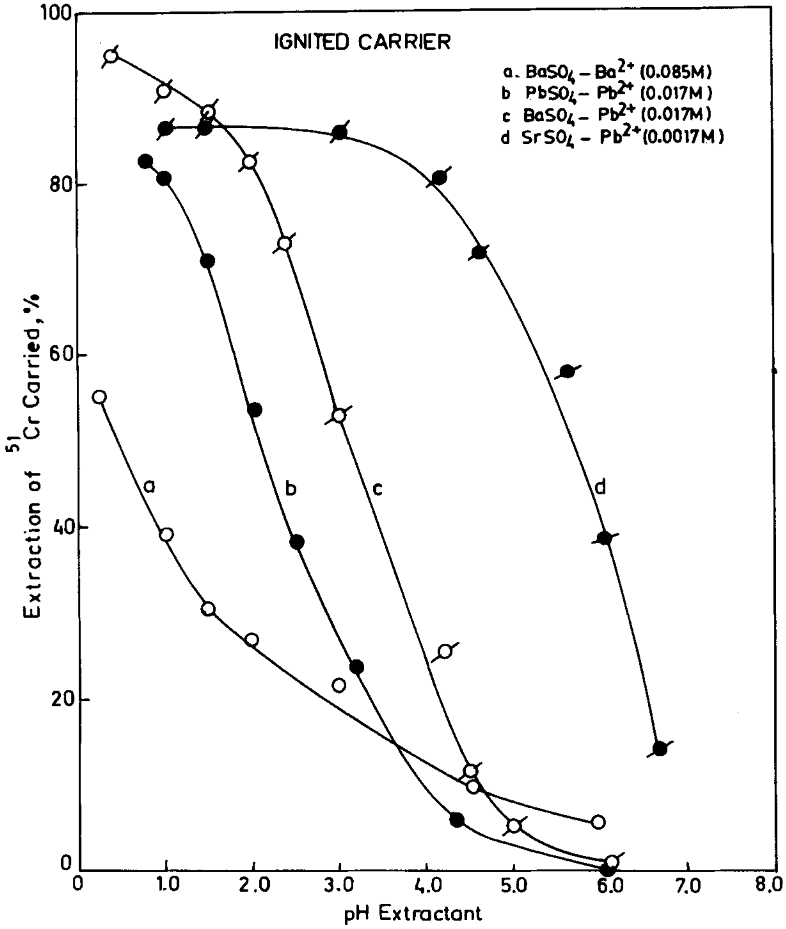

FIG. 4. Extraction vs pH.

dependent on the experimental conditions, e.g., pH and ionic composition of the solution. An attempt has been made to arrive at the optimum working conditions for the method. The factors that influence the primary adsorption as well as the desorption process have been studied and are reported as follows.

Carrying Efficiency as a Function of pH of the Aqueous Medium

The effect of varying the pH of the suspension medium on the carrying of tracers by different solids is presented in Figs. 1–3. From the data presented, the pH for maximum carrying can be chosen.

TABLE 1

Carrying Efficiency as a Function of Amount of Carrier (concentration of Pb^{2+} ions, 0.017 *M*; pH of the suspension, 4.30)

Amount of carrier × 10^3 *M*	Adsorption		
	$PbSO_4$	$BaSO_4$	$SrSO_4$
0.055	42.00	51.65	7.90
0.275	45.90	62.70	15.60
0.550	52.75	71.80	18.75
1.375	64.60	80.15	36.90
2.750	86.30	90.60	62.70
5.500	90.35	91.25	75.50
22.000	97.65	93.45	90.95
33.000	97.90	93.90	93.30
55.000	98.65	95.25	95.25
110.000	98.70	95.25	95.25

Adsorption/Desorption Efficiency as a Function of Lattice/Nonlattice Ion Concentration

Carrying efficiency as a function of lattice/nonlattice ions has been studied over a wide range of concentration of these ions, from which the concentration for maximum carrying can be chosen. The other aspect, i.e., the desorption efficiency as influenced by the concentration of the added nonlattice cations during carrying, has been studied, and the results are reported in Fig. 4 and Tables 3 and 4.

TABLE 2

Carrying Capacity of Adsorbents ($PbSO_4$ carrier, 0.055 *M*; [Pb^{2+}], nil; pH of the suspension, 3.50. $BaSO_4$ carrier, 0.055 *M*; [Pb^{2+}], 0.017 *M*; pH of the suspension, 4.30. $SrSO_4$ carrier, 0.055 *M*; [Pb^{2+}], 0.0017 *M*; pH of the suspension 4.30)

Amount of added Cr (mg)	Adsorption		
	$PbSO_4$	$BaSO_4$	$SrSO_4$
Nil	97.30	93.90	94.20
0.0001	96.25	93.45	94.05
0.001	96.55	92.90	93.90
0.002	95.65	93.50	95.55
0.005	95.20	93.80	96.25
0.010	95.10	94.50	96.70
0.050	96.50	94.70	96.80
0.250	98.25	95.80	97.50

TABLE 3
Influence of Nonlattice Cations on Desorption of $^{51}CrO_4^{2-}$ Ions on Barium Sulfate and Strontium Sulfate (amount of carrier, 0.055 *M*; maximum adsorption, 97–98.5%; activity washed off, negligible; pH of the eluant, 1.0)

Carrier	Added ions	pH for adsorption	% Desorption
$BaSO_4$	Pb^{2+} ions, 0.017 *M*	4.3	93.75
	Sr^{2+} ions, 0.017 *M*	6.9	35.20
$SrSO_4$	Pb^{2+} ions, 0.017 *M*	4.3	93.20
	Ba^{2+} ions, 0.017 *M*	6.9	41.40

Carrying Efficiency as a Function of Amount of Carrier

The influence of the quantity of carrier on the efficiency of carrying has also been examined under optimum experimental conditions. The results observed are presented in Table 1.

Carrying Capacity of Adsorbents

To establish the upper limit of the carrying capacity of the carriers, the amount of tagged species carried by an arbitrarily fixed amount of the carrier under otherwise identical experimental conditions has been determined radiometrically. The results are presented in Table 2.

In order to obtain maximum desorption of the carried activity, a systematic study has been made of the effects of the acidity of the extractant water on desorption of the carried activity. The tracer is adsorbed on a small quantity of carrier under the specified optimum conditions, and the adsorbed activity after washing under specified conditions (usually within

TABLE 4
Influence of Lead Ions on Desorption of $^{51}CrO_4^{2-}$ Ions on Barium Sulfate and Strontium Sulfate (amount of carrier, 0.055 *M*; pH for adsorption, 4.30; activity washed off, negligible; pH of the eluant, 1.0)

	$BaSO_4$		$SrSO_4$	
$[Pb^{2+}]$, (*M*)	% Carrying	% Desorption	% Carrying	% Desorption
0.00	89.45	35.00	—	—
0.00017	93.70	42.10	65.65	90.90
0.0017	94.35	46.50	95.20	90.00
0.0051	94.10	71.90	94.55	88.80
0.0085	94.85	90.00	96.00	86.10
0.017	95.30	93.80	96.10	85.70
0.085	95.30	93.85	96.20	84.65

1%) is subsequently desorbed with 12 mL of the aqueous solution of varying acidity. The percentage of desorption increases as the pH of the extractant water decreases (Fig. 4). Intimate contact of a little 0.1 *N* HNO_3 with the adsorbent surface is an essential requirement for efficient extraction of the adsorbed radioactivity. Three or four extractions are needed for the complete recovery of radioactivity.

Among the sulfates, barium sulfate and strontium sulfate carriers show very poor desorption when the carrying is done in the presence of their respective lattice cations. However, when desorption is carried out in the presence of nonlattice lead ions, it improves considerably. In the case of barium sulfate, the addition of lead ions significantly improves extraction. In the case of strontium sulfate, both the adsorption and desorption characteristics are improved in the presence of lead ions. The results are presented in Tables 3 and 4.

In the case of lead sulfate, as shown in Fig. 1, the optimum conditions for maximum adsorption (~98.4%) are added Pb^{2+} ions, 0.017 *M*; pH 4.30. By using 3 successive elutions, ~85% of the overall activity is desorbed with dilute HNO_3 of pH 1.0.

In the case of barium sulfate in the presence of barium ions, it is clear from Fig. 4 that the adsorbed activity cannot be leached out quantitatively even when the pH is lowered to 0.25. In view of the incomplete leaching, it was considered promising to carry out desorption studies on activity carried in the presence of a nonlattice cation e.g., lead ions. The results, presented in Table 3, indicate that in the presence of a certain quantity of Pb^{2+}, the desorption of the tracer becomes more or less quantitative. Therefore, the optimum concentration of lead ions has been determined and the results are shown in Table 4. As the lead ion concentration is increased from 0.0017 to 0.085 *M*, desorption increases from 46.5% to about 94%. Therefore, 0.017 *M* is the optimum concentration for lead ions.

With regard to strontium sulfate carrier in the presence of strontium ions, the carrier carries the chromate activity to only an insignificant extent (Fig. 3). Consequently, a desorption study was not conducted under these conditions. However, the deposition of the tracer can be improved to a quantitative level in the presence of added nonlattice cations (Pb^{2+} and Ba^{2+} ions). Also, the preliminary data presented in Table 3 reveal that for strontium sulfate, desorption becomes almost quantitative only in the presence of a certain quantity of lead ions. Therefore, the optimum conditions for lead ions have also been worked out experimentally in this case. The data presented in Table 4 show that a 0.0017 *M* lead concentration is the optimum for adsorption and desorption studies.

The experimental conditions needed to concentrate $^{51}CrO_4^{2-}$ tracer from extremely dilute aqueous solutions have been determined. The procedure seems to be quick and quite simple in operation, and it is likely to find applications involving concentration of the tracer as well as microgram quantities of the chromate species.

The results presented in Table 4 reveal that in comparison to carriers in the presence of their respective ions, $BaSO_4$–Pb^{2+} and $SrSO_4$–Pb^{2+} systems are more suitable for concentrating $^{51}CrO_4^{2-}$ species. It can be seen that activity adsorbed on barium sulfate and strontium sulfate is desorbed efficiently only if it is carried out in the presence of lead ions. This clearly indicates that the new surface formed by the incorporation of lead ions in the lattice of $BaSO_4$ or of $SrSO_4$ is more effective for both adsorption and desorption (Table 4). The use of a mixed surface has also been found to be more effective for the adsorption and desorption of uranium as compared to pure adsorbents (*16*). In the case of the $SrSO_4$–Pb^{2+} system, the phenomenon seems to be reversible, i.e., $^{51}CrO_4^{2-}$ activity adsorbed at pH 4.3 by this system is leached out with an eluant at the same pH. Reversibility of the phosphate adsorption isotherm with respect to the pH of the eluant has also been reported (*17*).

It should also be noted that under optimum experimental conditions, 200 mg of the $PbSO_4$–Pb^{2+} system carries 0.01 mg of chromium, whereas 155 mg of the $BaSO_4$–Pb^{2+} and 120 mg of the $SrSO_4$–Pb^{2+} systems carry about 0.004 mg of chromium (Table 2). In terms of radioactivity, the corresponding quantities initially present in a 12-mL aqueous solution are likely to be carried in a single operation to over 93% by the above quantities of these carriers. For larger volumes containing the same amounts of radioactive tracer, repetition of this operation is necessary. Unless the radioactive solution is extremely dilute, the charge-determining cations, added under specified experimental conditions, bring about an actual precipitation of chromate with the respective cations. The net carrying process is due to both precipitation and adsorption of the chromate ions.

On the basis of these experimental findings, there is a good possibility of concentrating the chromate species present in extremely dilute solutions by the use of lead sulfate in the presence of lead ions and also of barium sulfate and strontium sulfate in the presence of a nonlattice cation, i.e., Pb^{2+} ions. Three or four leachings are usually required for quantitative elution. The study has been extended to the presence of interfering ions.

The lower limit of estimation of the species is about 0.1 ppm. Therefore, this method of determination is not directly applicable to solutions of higher dilution, and the initial concentration is an essential prerequisite.

Freshly made adsorbents can be used for the concentration of a species from aqueous extracts. These surfaces carry the activity to a maximum extent at a much lower pH, but the percentage extraction with 0.1 *N* acid is only 15–20% of the adsorbed activity. Thus, freshly made precipitates of these carriers are of little use for concentrating the tracers of these species. However, in view of the large surface area and the low leaching properties, carriers in their freshly precipitated state can also find application for the disposal of radioactive wastes, especially when the activity involved is at a low concentration level.

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