

## Adsorption of Samarium on Activated Charcoal from Aqueous Solution

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**Summary:** Adsorption of samarium on activated charcoal has been studied as a function of shaking time, pH, concentration of adsorbate and temperature. Wavelength dispersive X-ray fluorescence spectrometer was used for measuring samarium concentration. Samarium adsorption obeys the Langmuir isotherm.  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and intercept of plot  $\ln K_D$  VS  $1/T$ . The influence of different cations and anions on samarium adsorption has been examined. The adsorption of other metal ions on activated charcoal has been studied under optimum condition to check its selectivity for samarium. Consequently samarium was removed from the aqueous solutions containing Cs, Sr, Nd, Zn, Cu, Co, Rb and Pr. More than 98% of adsorbed samarium on activated charcoal can be recovered with 50 ml of 3 M  $\text{HNO}_3$  solution.

### Introduction

The adsorption of samarium on solid is important for two reasons, first: preconcentration/enrichment view-point, second: it has numerous applications in glass, laser, electrical, chemical and nuclear industries. Previously its adsorption on tungsten [1,2], molybdenum [3,4], iridium [5,6], palladium [7], aluminium [8], calcium-hydroxyapatite [9] and alkaline earth carbonate [10] have been carried out, but no data is available for its adsorption on activated charcoal. In this communication an attempt has been made to study the adsorption behaviour of samarium on activated charcoal, which led to the determination of optimal conditions required for its preconcentration and separation.

### Results and Discussion

The adsorption of samarium on activated charcoal was studied as a function of shaking time; 10 ml solution containing 2000 mg/l of samarium was shaken with 100 mg of activated charcoal for different intervals of time ranging from 5 to 120 minutes. Fig. 1 shows the variation of  $K_D$  with shaking time. The  $K_D$  value increases with an increase of shaking time and attains a constant value around 30 minutes when adsorption equilibrium is established. 30 minutes shaking time was selected for all further studies.

Fig. 2 shows the influence of pH on the adsorption of samarium on activated charcoal. The

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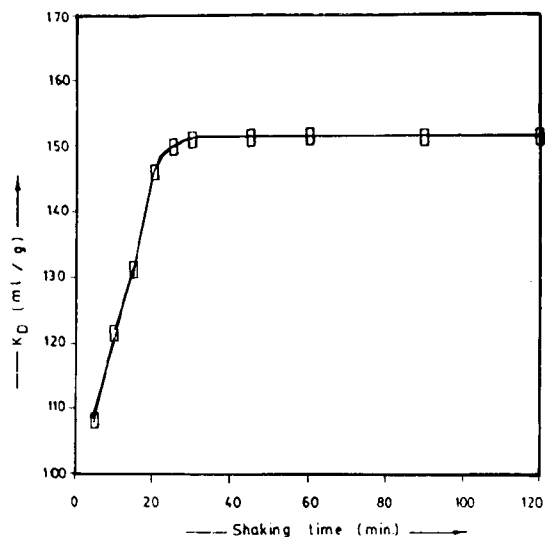


Fig. 1: Distribution coefficient ( $K_D$ ) as a function of shaking time for the adsorption of samarium on activated charcoal.

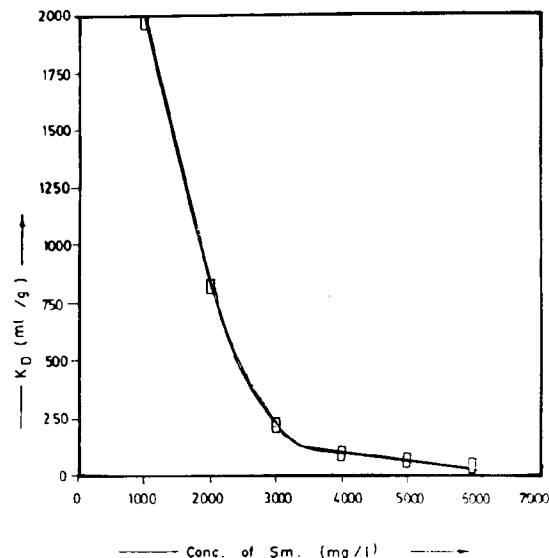


Fig. 3: Effect of samarium concentration on  $K_D$  for its adsorption on activated charcoal.

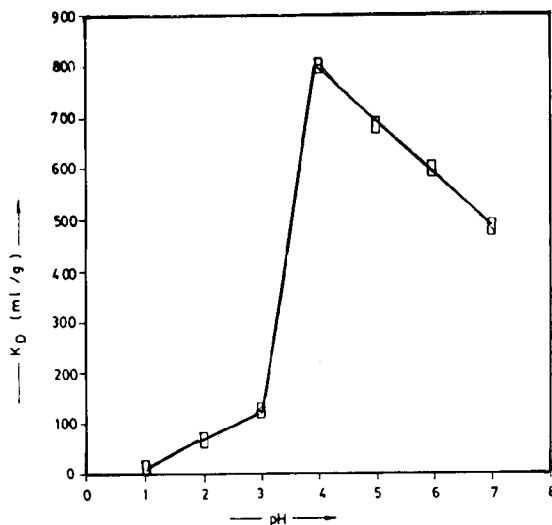


Fig. 2: Influence of pH on  $K_D$  for the adsorption of samarium on activated charcoal.

$K_D$  value increases with the increasing pH upto 4 and then starts decreasing. Maximum adsorption occurs at pH 4. Hence buffer of pH (Fluka, item No. 82560) was used for all further studies.

The effect of samarium concentration on the adsorption was studied under the optimized condition as determined before. The concentration of samarium was varied from 1000 mg/l to 6000 mg/l. The results in Fig. 3 shows that  $K_D$  values decrease

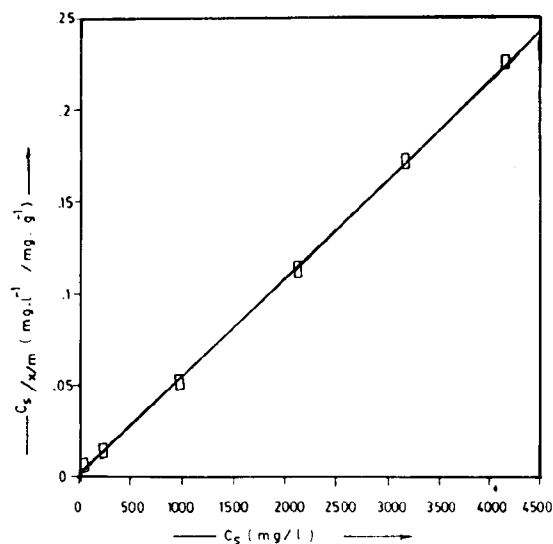


Fig. 4: Langmuir plot for samarium adsorption on activated charcoal.

as the samarium concentration increases, indicating that energetically more favourable sites became involved first. The results were then analyzed in term of Freundlich [14], Langmuir [15] and Dubinin-Rudush-Kevich (D-R) [16] isotherms. The data do not fit the Freundlich and D-R equations. A straight line was obtained in Fig. 4 when  $C_s/X/m$  was plotted against  $C_s$ , the equilibrium concentration of samarium. It follows that the adsorption of

samarium on activated charcoal obeys Langmuir isotherm.

The adsorption dependence of samarium on temperature was investigated. The temperature was varied from 10°C to 60°C in a step of 10°C, while

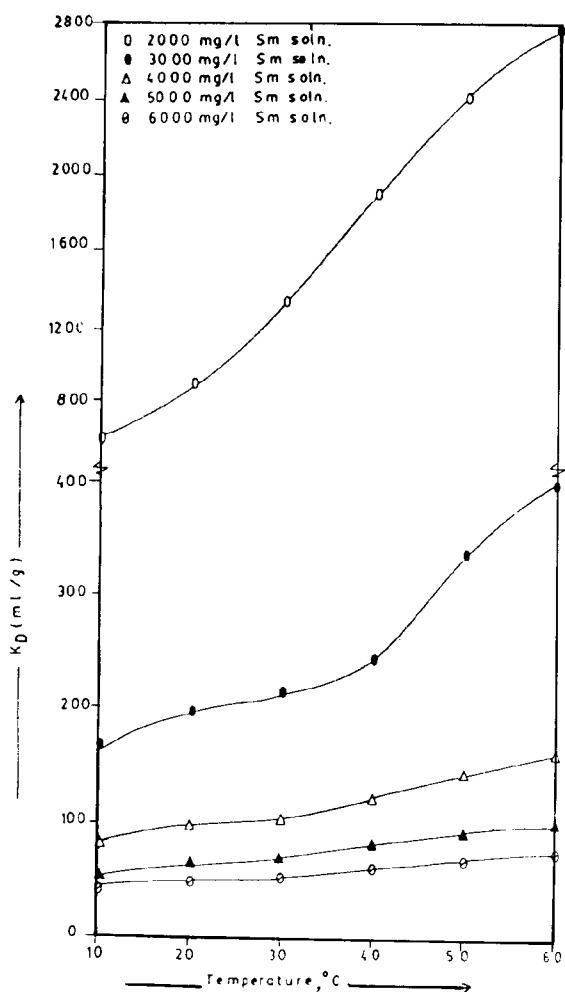


Fig. 5: Effect of temperature on KD for Sm adsorption on activated charcoal.

the other parameters were kept constant. Fig. 5 shows that KD values increase with the increase of temperature. This increase may be due to a negative temperature coefficient or to a steep simultaneous decrease of real adsorption of solvent [17]. The values of ΔH° and ΔS° are calculated from the slopes and intercepts of the linear variation of ln KD with reciprocal of temperature, 1/T, Fig. 6, using the relation

$$\ln KD = \Delta S^{\circ}/R - \Delta H^{\circ}/RT \quad (1)$$

The values of ΔH and ΔS° are given in Table 1. The free energy of specific adsorption, ΔG°, is calculated using the equation

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (2)$$

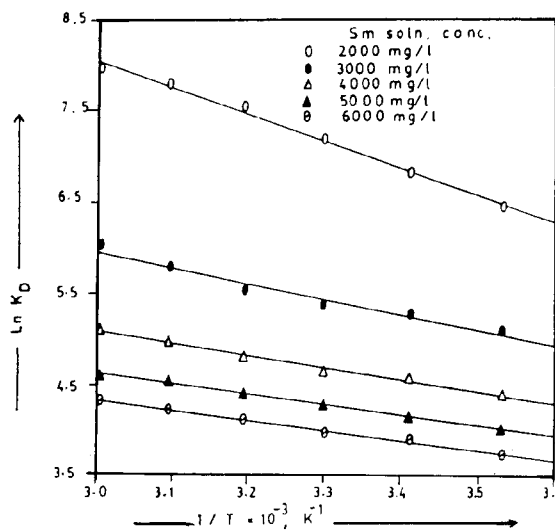


Fig. 6: Plot of lnKD vs 1/T for samarium adsorption on activated charcoal.

Table 1: Thermodynamic parameters for Sm adsorption on activated Charcoal

Sm Conc. (mg/l)	ΔH° KJ. mol <sup>-1</sup>	ΔS° KJ.K <sup>-1</sup> mol <sup>-1</sup>	ΔG° kJ.mole <sup>-1</sup>					
			283K	293K	303K	313K	323K	333K
2000	24.3517	0.1398	-15.2117	-16.6097	-18.0077	-19.4057	20.8037	-22.2017
3000	13.6183	0.0901	-11.8800	-12.7810	-13.6820	-14.5830	-15.4840	-16.3850
4000	10.6336	0.0742	-10.3650	-11.1070	-11.8490	-12.5910	-13.3330	-14.0750
5000	9.3865	0.0666	-9.4613	-10.1273	-10.7933	-11.4593	-12.1253	-12.7913
6000	9.1038	0.0633	-8.8101	-9.4431	-10.0761	-10.7019	-11.3421	-11.9751

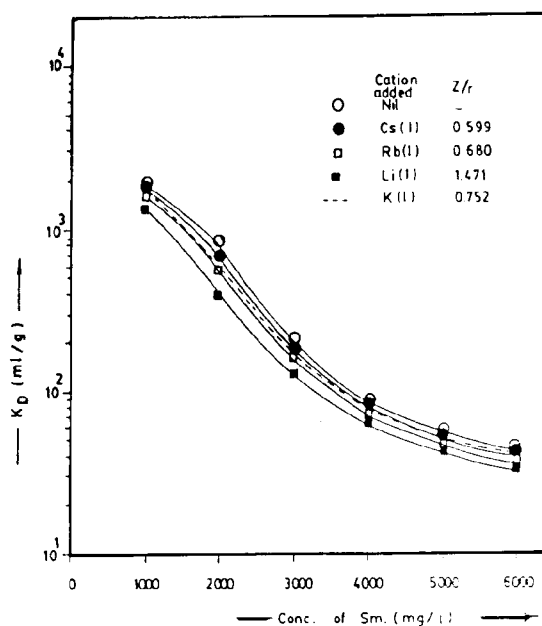


Fig. 7: Variation of  $K_D$  for samarium adsorption on activated charcoal in presence of monovalent cations.

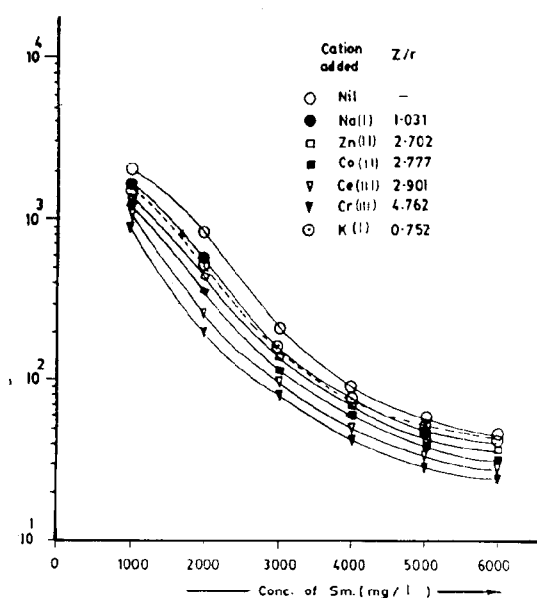


Fig. 8: Variation of  $K_D$  for samarium adsorption on activated charcoal in presence of cations of different valencies.

$\Delta G^\circ$  values are also given in Table 1. Positive values of  $\Delta H^\circ$  and decrease in values of  $\Delta G^\circ$  with rise in temperature show that the adsorption is more favourable at high temperature.

The influence of monovalent cations [Li(I), K(I), Rb(I), Cs(I)] and cations of different valencies [Na(I), K(I), Co(II), Zn(II), Ce(III), Cr(III)] on the adsorption of samarium on activated charcoal was investigated. The concentration of each cation was fixed as 1000 mg/l and samarium concentration was varied from 1000 mg/l to 6000 mg/l. The results of these investigations are shown in Figs. 7-8. It is seen that greater the ionic potential ( $Z/r$ ) of the added cation, the smaller is the adsorption of samarium, except potassium. Similar observations have been reported earlier [18].

To examine the adsorption behaviour of samarium on activated charcoal in the presence of acetate, thiosulphate, chloride, bromide, iodide, nitrate and EDTA, the concentration of each anion was fixed as 1000 mg/l and concentration of samarium was varied from 1000 mg/l to 6000 mg/l. The results are shown in Fig. 9. The acetate ions enhanced the adsorption of samarium while the other anions reduced the adsorption of samarium.

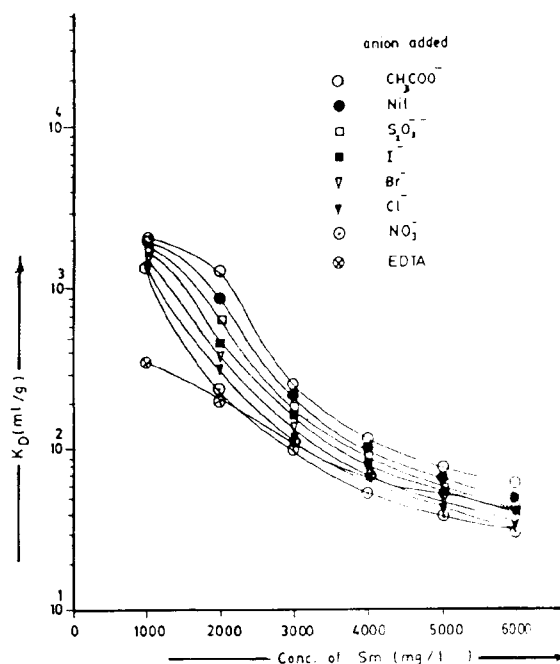


Fig. 9: Variation of  $K_D$  for samarium adsorption on activated charcoal in presence of some anions.

To check the selectivity of activated charcoal for adsorption of samarium, the adsorption of Gd,

Er, Eu, Nd, Ce, Pr, Dy, La, Zn, Cr, Cu, Co, Mn, Rh, Sr, Ba, Ru, Cs, U, Y, Cd and Rb on activated charcoal was examined under the optimum conditions for samarium. The results are given in Table 2. It is obvious from the data that Er, Eu, Gd, Dy, U, La, Ce and Ba have considerably high value of  $K_D$ . So they would be co-adsorbed along with samarium on activated charcoal. Y, Cr, Ru, Cd, Mn, Cs, Sr, Nd, Zn, Cu, Co, Rb and Pr are poorly adsorbed, hence separation of samarium from these metals can be achieved. The separation factor for samarium is larger in the presence of Pr, Rb, Co, Cu, Zn, Nd, Sr and Cs; because they have much lower  $K_D$  values. The separation of samarium in presence of these metals is shown in Fig. 10.

Table 2: Distribution coefficient ( $K_D$ ) values of other metals on activated charcoal at optimized conditions for Samarium

Metal*	$K_D$ (ml/g)**
Er	847.87
Eu	536.94
Gd	486.51
Dy	353.51
U	217.97
La	138.95
Ce	100.61
Ba	96.08
Rh	43.78
Y	29.53
Cr	24.84
Ru	23.15
Cd	22.47
Mn	22.17
Cs	17.23
Sr	15.31
Nd	14.71
Zn	13.12
Cu	12.93
Co	12.61
Rb	6.67
Pr	6.55

\*Concentration of all metals fixed at 2000 mg/l.

\*\*The order of entries is on the basis of decreasing  $K_D$

The feasibility of using activated charcoal for preconcentration of samarium was further assessed by elution study. This study was performed with 3M  $HNO_3$  solution and the result is shown in Fig. 11.

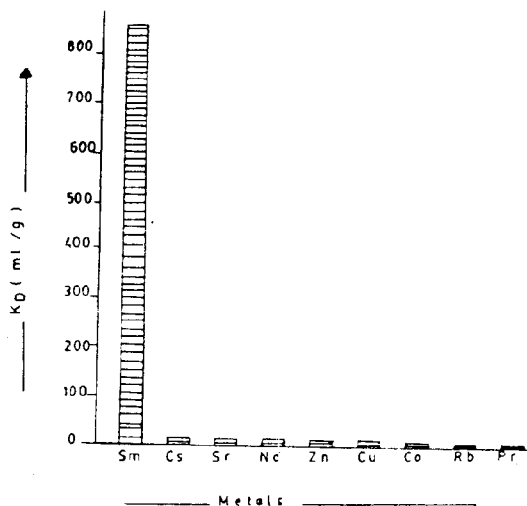


Fig. 10:  $K_D$  of Sm and other metals from a mixture containing Sm, Cs, Sr, Nd, Zn, Cu, Co, Rb and Pr.

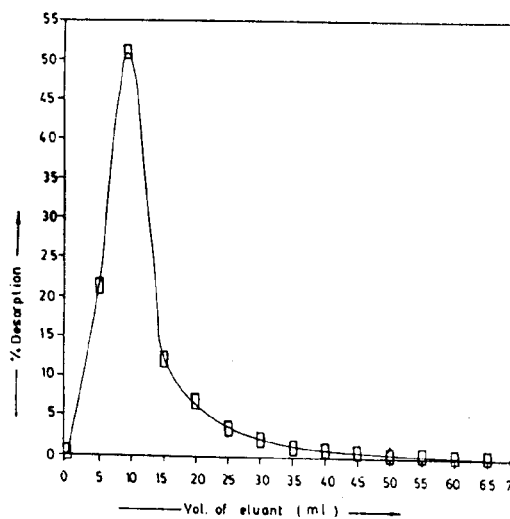


Fig. 11: Elution of adsorbed samarium from activated charcoal with 3M  $HNO_3$  solution.

### Experimental

#### Chemicals and reagents

Activated charcoal supplied by M/S BDH (item No. 33032) and samarium nitrate (99.999%) supplied by M/S Rare Earth Product, were used, while buffer solutions of different pH supplied by M/S Fluka were used for pH studies.

### Instruments

Siemen's wavelength dispersive X-ray fluorescence spectrometer (WDXRFS) SRS-200 was used with followed attachments: Cr X-ray tube; soller slit with angular divergence  $0.15^\circ$ ; LiF (100) crystal; NaI(Tl) scintillation counter, linked through an universal interface, LC-200 to a PDP-11/04 computer. The pH measurements were made with a digital pH meter-605 from M/S Metrohm. Edmund Buhler-SM25 shaker was used for shaking at a constant speed of 150 revolutions per minute.

### Procedure

Adsorption measurement was carried out by a batch technique at room temperature ( $18 \pm 1^\circ\text{C}$ ) except where other wise specified. A known amount of activated charcoal in 250 ml reagent bottles containing 10 ml samarium solution of various concentration was shaken for a given time period. The solution was then filtered and the concentration of samarium in filtrate was measured by WDXRFS. The sample solution was presented to the spectrometer in a 0.1 mm thick walled polyethylene bottle [11,12]. The distribution coefficient ( $K_D$ ) was computed in the usual method [13].

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