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Solvent Extraction of W(VI) with Malachite Green into Nitrobenzene

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A rapid and selective method has been developed for the extraction of W(VI) with malachite green into nitrobenzene. The effect of various parameters on the extraction coefficient value such as effect of pH, time of equilibration, effect of various cations and anions have been evaluated. The stoichiometry of metal to reagent determined by the method of substoichiometric extraction was found to be 1 : 1. It was further supported by the slope ratio method.

INTRODUCTION

Malachite green has been used for the solvent extraction of a large number of metal-ions such as Sn(II)[1], Zn(II)[2] and Cd(II)[3]. The study on sensitive colour reaction of W(VI) thiocyanate-malachite green system in the presence of polyvinyl alcohol by spectrophotometric method[4], and use of malachite green for the detection of tungsten[5] has been reported. However, the extraction of W(VI) with this reagent for radiochemical separation has not been reported in the literature. The present work describes a rapid and selective method for the extraction of W(VI) with malachite green into nitrobenzene. Ideal conditions for the extraction have been established.

EXPERIMENTAL

Reagents and Chemicals: All the chemicals and reagents used were of A.R. Grade. ^{185}W and the isotope used for studying the interference of other cations were supplied by BRIT, Bombay. A stock solution of W(VI) was prepared by dissolving A.R. Grade Na_2WO_4 in distilled water containing a little NaOH. Solutions of anions were prepared by dissolving appropriate salts in distilled water and that of cations were prepared in the same way, but 5 mL of concentrated HCl was added to the solution, wherever required. The strength of these solutions was determined by the standard method given in Vogel[6]. The solution of reagent malachite green oxalate (Loba Chem), used in the extraction studies was prepared by dissolving appropriate amount of the reagent in distilled water. The purity of reagent was checked by determining its melting point (164°C) and it was found to be in agreement with that reported in the literature.

Instrumentation: Gamma-emitters were counted on a single-channel pulseheight analyzer in conjuction with a 3.5 cm × 3.5 cm NaI(Tl) well-type crystal detector. Beta-emitters were counted on a thin end window type G.M. counter in conjuction with a decade scaler, high voltage unit and a timer.

Extraction Procedure: In a separating funnel, 1.5 mg of W(VI) labelled with ^{185}W was taken 0.5 mL of 1% aqueous solution of malachite green was added. The volume of the solution was made to 15 mL after adjusting the pH of the solution with HCl or ammonia. The mixture was equilibrated for 5 minutes with 15 mL of nitrobenzene. The phases were allowed to separate and a 2 mL aliquot of each phase was taken in a planchet which was evaporated to dryness and was taken for counting on a G.M. counter. The extraction coefficient value E was calculated using the equation:

$$E = \frac{\text{Activity of 2-mL aliquot of the organic phase}}{\text{Activity of 2-mL aliquot of the aqueous phase}}$$

RESULTS AND DISCUSSION

Effect of pH, time of equilibration and solvents: From Table-1 it can be seen that a maximum E value of 85 was obtained for the extraction of W(VI) with malachite green into nitrobenzene at a pH of 8.5 and an equilibration time of 5.0

TABLE-1
EFFECT OF pH AND TIME OF EQUILIBRATION ON THE EXTRACTION COEFFICIENT VALUE OF W(VI) WITH MALACHITE GREEN INTO NITROBENZENE

pH	Extraction coefficient E	Percentage extraction %E	Time of equilibration in min.
2.0	1.0	47.49	5.0
3.0	2.0	66.66	5.0
4.0	3.3	76.74	5.0
5.0	11.0	91.66	5.0
6.0	20.0	95.23	5.0
7.0	22.0	95.65	5.0
7.5	36.0	97.29	5.0
8.0	71.0	98.61	5.0
8.5	85.0	98.84	5.0
8.5	80.0	98.75	5.0
8.5	75.0	98.68	5.0
9.0	44.0	97.79	5.0
10.0	00.07	6.54	5.0
8.5	20.0	95.23	3.0
8.5	30.0	96.77	4.0
8.5	80.0	98.76	5.0
8.5	49.0	98.00	6.0
8.5	45.0	97.82	7.0
8.5	44.0	97.77	8.0

minutes. The extraction of W(VI) into different organic solvents was ascertained and it was found that the extraction coefficient value decreased in the following order.

Nitrobenzene > chloroform > nitromethane > iso-amyl alcohol
E = 80.0 24.0 04.0 1.7

> 1, 2-dichlorobenzene > ethyl methyl ketone > heptanol
E = 0.4 0.33 0.20

> 4-methyl pentane-2-one > 1-butanol > ethyl acetate
E = 0.18 0.16 0.02

> toluene > isoamyl acetate = benzene
E = 0.014 0.008 0.008

> carbontetrachloride > xylene > heptane
E = 0.0063 0.005 0.004

Propanol, pyridine and ethylene glycol were found to be miscible with the organic phase. Hence in all further studies nitrobenzene was used as a solvent.

Effect of Anions: The effect of various anions on the percentage extraction of W(VI) revealed that the extraction was better than 98% when 100 mg each of chloride, sulphate, sulphite and thiourea, 25 mg of bromate, 10 mg each of EDTA, thiosulphate, carbonate, perchlorate, oxalate, sulphide, bromide, nitrite, bicarbonate, phosphate and hypophosphite were present. Thiocyanate, acetate, iodide, cyanide, citrate and tartrate interfered, but their interfevence was removed by expelling each one of them with concentrated HNO_3 and HCl, whereas the interference of nitrate was removed by expelling it with concentrated HCl prior to the extraction of W(VI).

Separation factor: The separation factor for other elements in the extraction of W(VI) was determined and it was found to be highly selective. Of the elements studied Cs(I), Na(I), Tl(I), Cl(I), Rb(I), Cu(II), Zn(II), Mn(II), Co(II), Sc(III), La(III), Cr(III), Eu(III), As(III), Ce(IV),.Se(IV), Sn(IV), P(V), As(V) and Sb(V) were extracted to the extent of less than 1.0%. Ba(II), Ca(II), Fe(II) and In(III) were extracted to the extent of less than 2.0%. K(I), Ag(I), Cd(II), Ce(III), Ru(III), Au(III), Ir(III) and Zr(VI) were extracted between 2.0 to 10.0%. Fe(III), Te(IV) and Cr(VI) were extracted to more than 25% but they were suppressed to below 10% by reducing them with hydrazine hydrate, hydroxylamine hydrochloride and boiling with HCl and H_2O_2 respectively. Pd(II) and Sn(II) were extracted to more than 50%, but they were suppressed by masking Pd(II) with 100 mg of thiourea and oxidising Sn(II) to Sn(IV) with concentrated HNO_3. Tc(VII), Mo(VI) and Hg(II) were extracted to more than 96%. Tc(VII) was masked with 100 mg of hydroxylamine hydrochloride, whereas Mo(VI) and Hg(II) were removed by precipitating W(VI) as tungstic acid, and rejecting Mo(VI) and Hg(II) in the supernatant after centrifugation and then dissolving tungstic acid in ammonia prior to the extraction of W(VI).

Stoichiometry: The stoichiometry of the extracted species determined by the method of substoichiometric extraction was carried out as follows: In a series of separatory funnels, increasing amount of W(VI) labelled with ^{185}W was taken. 5 mL of water containing 50.38 mg of malachite green was added. The volume of the solution was made to 15 mL with distilled water, after adjusting the pH of

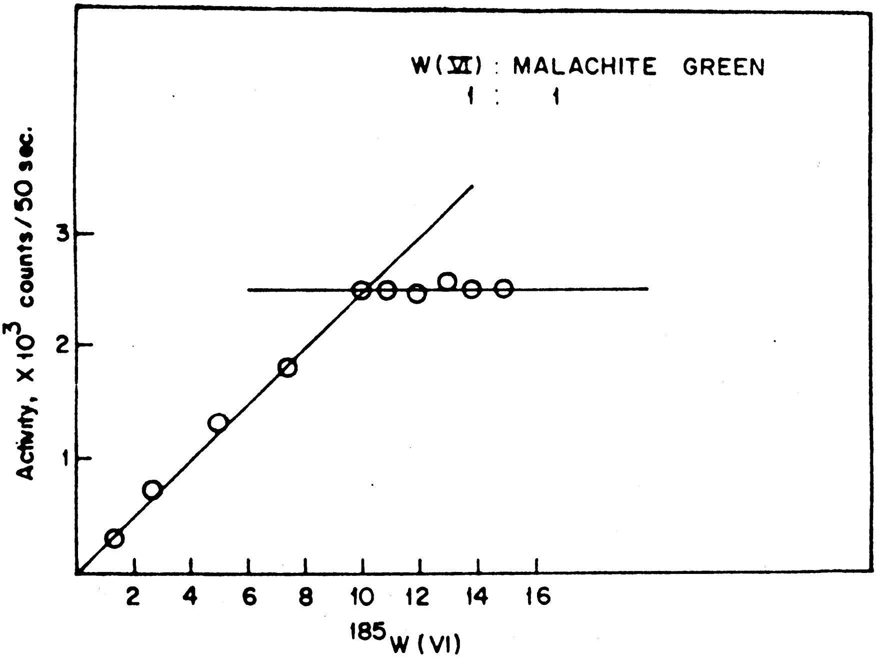

Fig. 1. Reproducibility of substoichiometric extraction of $^{185}W(VI)$ with malachite green into nitrobenzene

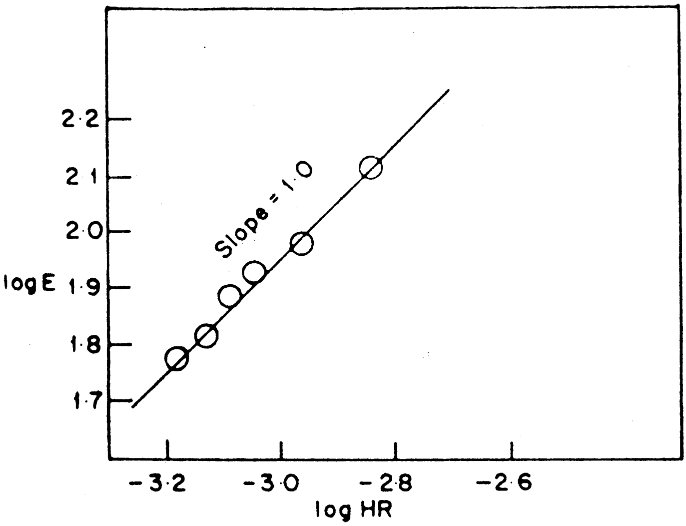

Fig. 2. Slope ratio method: Effect of reagent concentration on the extraction coefficient value of W(VI) with malachite green into nitrobenzene.

the solution to 8.5. The aqueous phase was equilibrated for 5.0 minutes with 15 mL of nitrobenzene. The phases where allowed to separate and a 2 mL aliquot of the organic phase was taken in a planchet which was evaporated to dryness and was taken for counting on a G. M. counter. The activity *i.e.* counts/50 sec. of 2 mL aliquot of the organic phase was plotted against the amount of W(VI) taken (Fig. 1). From Fig. 1, it can be seen that the activity increased with an increase in the concentration of W(VI), till it was subequivalent to the reagent added. After reaching an equivalence point, the activity remained constant with an increase in the concentration of W(VI). A break was observed at the equivalence point, corresponding to the metal: reagent in the ratio of 1:1. This was further supported by the slope ratio method (Fig. 2).

Decontamination factor (Table-2) for different elements was determined at substoichiometric level and was found to be greater than 10^2 for most elements.

Reproducibility of the extraction was found to be 6.25%.

TABLE-2
DECONTAMINATION FACTOR FOR DIFFERENT ELEMENTS

D.F. greater than	Elements	
	With milligram amounts of carrier	Without milligram amounts of carrier
10^5	Rb(I), Cs(I), Ag(I), Cl(I), Co(II), Cd(II), Hg(II)*, Sc(III), In(III), Ca(II), Se(IV), S(VI), Mo(VI)*	Rb(I), Cs(I), Ag(I), Cl(I), Co(II), Cd(II), Hg(II)*, Sc(III), In(III), Ca(II), Se(IV), S(VI), Mo(VI)*
10^3	Fe(II), Sn(II)*, Fe(III), Sn(IV), Sb(V)	Fe(II), Sn(II)*, Sn(IV), Sb(V), Tc(VII)*
10^2	Tl(I), Zn(II), Ba(II), Mn(II), Eu(III), Sb(III), Ru(III), Cr(III), Ce(III), Ce(IV), Zr(IV), Ir(III), P(V), Cr(VI)*	Fe(III), Tl(I), Zn(II), Ba(II), Eu(III), Ru(III), Sb(III), Cr(III), Ce(III), Ce(IV), Zr(IV), Ir(III), P(V), Cr(VI)*
10^0	Mo(VI), Hg(II), Sn(II), Cr(VI)	Mn(II), Mo(VI), Hg(II), Sn(II), Cr(VI), Tc(VII).

*after treatment.

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