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# Hexanitrodiphenylamine as Reagent for the Removal of Radioactive Cesium from Aqueous Solutions

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**KEY WORDS:** asbestos, cesium, hexanitrodiphenylamine, potassium hexacyanoferrate, radioactive waste.

A method for the removal of radioactive contamination from low and medium radioactive liquid waste is proposed. It consists of adsorbing reagents, with specific affinity for the cations to be removed, onto water insoluble supports of technical grade which can then be used as ion exchangers or "solid reagents".

This was verified with hexanitrodiphenylamine adsorbed on asbestos, vermiculite, alumina, kaolinite and bentonite to remove Cs-137 and Cs-134 from liquid wastes. This reagent, although widely used for the extraction of cesium, is not very efficient in the method suggested here. Much better decontamination results were achieved with potassium hexacyanoferrate adsorbed on asbestos.

## INTRODUCTION

In many liquid radioactive wastes one finds Cs-137, —a gammaemitter with a half life of 30 years. Cs is difficult to remove from these solutions by conventional precipitation methods used for liquid waste treatment. Therefore we attempted to modify a known analytical procedure for this purpose.

The anion of hexanitrodiphenylamine (syn. dipicrylamine), denoted by HDPa in the subsequent text is known to form ion pairs with alkali metal cations.<sup>1</sup> The association constants of these ion pairs increase so that, from potassium on, the salts are water insoluble. Therefore HDPa found use as a

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specific reagent for the determination of potassium and, in its absence, of cesium.<sup>2</sup>

The water soluble salts of ammonium-, lithium- or magnesium-DPA are used for the direct removal of the insoluble salts from aqueous solutions by precipitation<sup>3</sup> and also for the gravimetric determination of K and Cs.<sup>4</sup> In an indirect method HDPA is used to remove Cs from aqueous salt solutions. The Cs-DPA salt is extracted into a polar organic solvent, mainly nitrobenzene. Most of the work in this area has been done by Kyrš *et al.*<sup>5</sup> The same method has been also applied by other research groups<sup>6</sup> and serves mainly to remove, regain and separate radioactive Cs from other fission products.

Yet another possible way to use HDPA for the removal of Cs from aqueous solutions is to adsorb it on a solid support which is then used as a chromatographic column. For very low amounts, of about 100  $\mu\text{g}$  Cs, this method has been successful using Polytrifluorochloroethylene (Kel-F) as the solid support.<sup>7</sup> In the present work our aim was to investigate this possibility and apply it to higher concentrations.

## PHYSICAL AND ANALYTICAL PROPERTIES OF HDPA AND ITS Cs SALT

Cs-DPA forms triclinic crystals.<sup>8</sup> A crystal-optical study of several metal-DPA compounds indicates that their properties are similar, being largely determined by the anion.<sup>9</sup> Another study of the electronic, vibrational and pmr spectra of these compounds indicates that this anion has a uniform charge distribution among the nitro groups.<sup>10</sup> The uv-vis spectrum of HDPA is obviously strongly pH dependent. Schill and Danielsson,<sup>11</sup> report that the compound, free from contaminating impurities has a  $pK_a = 2.8$  and isosbestic point at 340  $m\mu$ . The maximum absorption of  $\text{DPA}^-$  is at 430  $m\mu$  in water (phosphate buffer). In methylenechloride this absorption shifts to 420  $m\mu$  and coincides with the maximum absorption of an  $\text{NH}_4$ -DPA complex which has  $\epsilon = 3.1 \cdot 10^4 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ . Kourim *et al.*<sup>4</sup> also report the maximum absorption for the  $\text{DPA}^-$  anion at 425  $m\mu$  with  $\epsilon = 2 \cdot 10^4 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ . The absorption maxima of Cs, Rb-, K- and  $\text{NH}_4$ -DPA salts coincide with that of the anion (as measured in a basic solution) and all have  $\epsilon$  values of  $2.5 \cdot 10^4 \text{ l} \cdot \text{mole} \cdot \text{cm}^{-1}$ . In ether the absorption maximum is shifted to 372  $m\mu$  and the  $\epsilon$  lowered to  $1.5 \cdot 10^4 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ . This 420  $m\mu$  absorption band has been used for microgram determinations of HDPA,<sup>12</sup> which indicates its sensitivity. Identification and separation of HDPA from other aromatic nitro compounds has been made by TLC.<sup>13</sup> IR spectra of HDPA and its pyridine complex have been reported by Kapoor *et al.*<sup>14</sup> They give a detailed assignment of the absorptions of the parent compound and their shifts as caused by the complex formation.

## EXPERIMENTAL

HDPa (Fluka) was recrystallised from acetone and air dried. All other reagents were of analytical purity and were used as such.

Adsorbents used were of technical grade: Asbestos (Fluka), Aluminium dioxide Typ G2 (Woelm), Bentonite, Kaolinite and Vermiculite raw and expanded (Centram SA Zürich).

Adsorption isotherms were done in batches of 1.0 and 2.0 g adsorbent equilibrated with 100.00 ml solution of varying concentration of HDPa. They were equilibrated overnight at 25°C in a thermostat controlled shaker. The adsorbent was separated from the solution by centrifugation and the concentration of HDPa determined spectrophotometrically. In aqueous solution of pH 12 we found an unchanging maximum at 426 mμ with  $\epsilon = 2.62 \cdot 10^4 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ .

For the removal of cesium from aqueous solutions, the "Reactive adsorbent" was prepared by equilibrating it overnight with a solution of HDPa in dioxane and flash evaporating the solvent. Then the solid was washed with water and dried. For comparison purposes the concentration ratios were 1 mMole HDPa/1 g adsorbent.

The experiments for the removal of cesium were also done in batch. A solution of CsCl with Cs-137 as tracer was used. The concentration of cesium remaining in solution and that of cesium removed by the Reactive adsorbent were followed by measuring the radioactivity of the tracer. The most effective Reactive adsorbents were used to remove Cs-137 and Cs-134 from an aqueous solution which resulted from the decontamination of metallic tabs that had been irradiated in the ducts of Dragon, a HTGR (High Temperature Gas Cooled Reactor) at Winfrith (England).

## RESULTS

The results of the batch adsorption experiments were shown to fit the logarithmic form of Freundlich's equation

$$\log m = \log k_1 + 1/n \log C_{\text{eq}} \quad (1)$$

where  $m$  is the quantity of adsorbed species per unit weight of adsorbent and  $C_{\text{eq}}$  is the concentration of the adsorbed species in solution when equilibrium has been reached.

The parameters of Eq. (1) calculated for the systems HDPa-asbestos and HDPa-Al<sub>2</sub>O<sub>3</sub> in dioxane, methanol and water are summarized in Tables I and II respectively.

Reflectance IR spectra of the HDPa-Adsorbents were taken.<sup>15</sup> The uptake of solvent by the adsorbent due to the mixing of the solution with the dry adsorbent was checked. In the case of HDPa-asbestos, a nitrogen analysis

TABLE I

HDPa-Asbestos results of batch adsorption experiments, checked to fit Freundlich's equation  
 $\log m = \log k_1 + 1/n \log C_{eq}$

Parameter	Water	Methanol	Dioxane
$\log k_1$	1.18	-0.277	-1.52
$1/n$	1.07	0.597	0.0895
Correlation coefficient	0.998	0.992	0.967
Nr. of mes.	7	7	6
$S^\dagger (\log k_1)$	$9.24 \cdot 10^{-2}$	$1.12 \cdot 10^{-1}$	$3.96 \cdot 10^{-2}$
$S^\dagger (1/n)$	$2.87 \cdot 10^{-2}$	$3.45 \cdot 10^{-2}$	$1.18 \cdot 10^{-2}$

$\dagger S$  = square root of variance.

TABLE II

HDPa-Alumina results of batch adsorption experiments, checked to fit Freundlich's equation  
 $\log n = \log k_1 + 1/n \log C_{eq}$

Parameter	Methanol	Dioxane
$\log k_1$	0.686	0.0243
$1/n$	1.08	0.450
Correlation coefficient	0.999	0.993
Nr. of meas.	7	16
$S^\dagger \log k_1$	$6.37 \cdot 10^{-2}$	$4.83 \cdot 10^{-2}$
$S^\dagger (1/n)$	$2.01 \cdot 10^{-2}$	$1.48 \cdot 10^{-2}$

$\dagger S$  = square root of variance.

Note: There is no uptake of HDPa by alumina from water.

(Kjeldahl) of the HDPa adsorbed from all three solvents indicated no solvent uptake. Also NaCl added to the aqueous solution of HDPa showed no change in concentration (both  $\text{Na}^+$  and  $\text{Cl}^-$ ) after a batch adsorption experiment. With  $\text{Al}_2\text{O}_3$  the nitrogen analysis was unsuccessful, and with bentonite and kaolinite, about 10% of the NaCl added to the HDPa solution was adsorbed by them.

Therefore, in all cases,  $m$  was calculated from the difference between initial and equilibrium concentrations per 1.0g adsorbent. Since the adsorbent was always equilibrated with 100.0 ml solution, the error due to a possible uptake of solvent is most probably within the error of the analytical procedures.

In Table III maximum adsorption values for HDPa by different substrates and from different solvents are compared. These values were either obtained

TABLE III  
Maximal adsorption values for HDPA from different solvents

Adsorbent	mMole HDPA/1.0 g Adsorbent, from Solvent		
	Water	Methanol	Dioxane
Asbestos	0.02	0.04	0.03
Al <sub>2</sub> O <sub>3</sub>	n.a.	0.01	0.1
Bentonite	0.04	—	—
Kaolinite	0.02	—	—
Vermiculite raw)	n.a.†	n.a.†	n.a.†

†n.a. —no adsorption takes place.

through extrapolation of the respective adsorption curves or were measured in batch experiments with solutions 0.01 M in HDPA. The effectiveness of the HDPA-Adsorbent as to the uptake of cesium from aqueous solutions, was compared in batch experiments. Different amounts of the reactive adsorbent were equilibrated with solutions ranging from 2 mM–5 mM Cs/100 ml. The mean results are collected in Table IV.

In Table V are the results which demonstrate the removal of radioactive cesium from aqueous solution. These low activity water solutions resulted from the first stage of removal of radioactive contamination from metals.

## DISCUSSION

The purpose of this investigation was to devise a simple, versatile and economical method for the removal of radioactive contamination from large volumes of liquid waste of medium and low activity. Because Cs-137 released to the environment from nuclear power stations and is retained and highly concentrated by some soils and sediments, it represents a significant potential hazard for man.<sup>16</sup> The use of specific reagents, which strongly bind the isotope to be removed and are themselves attached to water insoluble supports, should make its removal possible. In this manner one eliminates the use of excess reagent needed, for example, for precipitation. Another advantage is that the radioactive contamination is already in a solid and concentrated form ready for disposal.

We chose HDPA as the specific reagent because it has already been used for similar purposes.<sup>5, 6, 7</sup>

Independent of support, the highest capacity is achieved if HDPA is

TABLE IV  
Uptake of cesium from aqueous solution by the reactive reagents: HDPA-adsorbent prepared by flash evaporating the solvent equilibration

HDPA-Adsorbent	Alumina	Asbestos	Bentonite	Kaolinite	Vermiculite (raw)	Vermiculite (expanded)
mM Cs/gr	0.3	0.3	0.5	0.05	0.12	0.5

TABLE V  
Decontamination of Cs in low radioactive liquid waste

Aqueous Isotope	Remaining radioactivity and decontamination factors after treatment with					
	HDPA-Alumina		HDPA-Asbestos		K <sub>2</sub> Zn <sub>3</sub> (Fe(CN) <sub>6</sub> ) <sub>2</sub>	
	nCi/l	K <sub>D</sub>	nCi/l	K <sub>D</sub>	nCi/l	K <sub>D</sub>
Sb-125	400	1.4	350	1.1	350	1.1
Cs-134	740	1.2	530	1.4	20	37
Cs-137	1900	1.2	1450	1.3	50	38
Mn-54	400	1.4	110	3.6	280	1.4
Co-60	70	3.5	2	35	25	2.8

adsorbed from dioxane (see Table III). Also, each of the exponents  $1/n$  in Freundlich's adsorption isotherm has the lowest value when adsorbed from dioxane. When the value of  $1/n$  approaches zero the available surface for adsorption is almost covered.

IR spectra do not give any clue as to how the HDPA is attached to the adsorbent. Reflectance IR spectra were taken but the concentration of adsorbed HDPA is too low to show any significant changes. The relatively high adsorption from dioxane is due to the excellent solubility of the acid form of HDPA in this solvent. In methanol and water only the conjugate base DPA<sup>-</sup> is reasonably soluble. It is this anion that reacts directly to give the insoluble salts. As seen from Tables I and II its adsorption is smaller. The uptake of HDPA by a support can be increased if the solvent (dioxane) is flash evaporated after equilibration. This is evident from Table IV where the uptake of cesium from aqueous solutions by supports prepared in this manner is higher than the maximum capacities of the adsorbents with respect to HDPA (see Table III).

HDPA has some drawbacks for the application we considered. It cannot be used in the presence of excess cations, e.g. potassium that also form water insoluble salts with HDPA and do not have to be removed. HDPA is not adsorbed strongly by the supports so that, for prolonged contact times and in large volumes of water, some of the reagent is leached out. For this same reason the particular HDPA supports described here cannot be used in columns for the removal of cesium from solution: therefore we used them in batch experiments.

In Table V are given the concentrations of radioactive cations before and after stirring a low activity solution with HDPA adsorbed on solid supports. The decontamination factors in these solutions are not good for the reasons already mentioned. However, by using potassium-zinc-hexacyanoferrate(II)- $K_2Zn_3(Fe(CN)_6)_2$ , which is known to exchange cesium,<sup>17</sup> we prepared a "reactive adsorbent"<sup>18</sup> from which the active compound is not leached out and which is much more effective than HDPA. The corresponding decontamination factors are included in the same table.

In this paper our aim has been to demonstrate the basic idea of using a reagent which is bound physically rather than chemically to a solid support, for the removal of unwanted traces of species from solution. Work is under way to apply this idea to more suitable reagents and other radioactive cations.

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