

studied to establish whether the observed pulmonary alterations were related to the exposure to rare earths present in cored arc light carbon.

Neutron activation analysis (NAA) has been used for the determination of rare earths in lung and lymph node biopsies of the worker as well as a control group. The results show a clearly abnormal presence of rare earths in the biopsies of the worker. The pulmonary concentrations of the worker for La, Ce, Nd and Sm were 45.6, 166.5, 57.5 and 4.55 ppm respectively whereas the corresponding concentrations of the controls were 0.017, 0.071, 0.046 and 0.0025. The differences in Eu, Tb, Yb and Lu concentrations were lower than these but were consistently higher than the values in the lungs of the control group. The amounts of La, Ce, Nd and Sm in lymph nodes of the worker were also significantly higher than in the controls. The differences, however, are lower when compared with the lung. Results on Eu, Tb, Yb and Lu in lymph nodes are judged as not being sufficiently definite to establish differences between the worker and the control group. These findings appear particularly important if correlated to the severe pneumoconiosis in the worker as substantiated by clinical and chest X-ray analysis.

Determination of 20 elements, besides the rare earths, in the lung and lymph nodes of the subject examined shows no significant differences as compared to the control group.

The estimated radiological dose due to the natural thorium, which is generally present as an impurity of rare-earth compounds, and the radioactive, naturally-occurring ^{138}La , $^{144+150}\text{Nd}$ and ^{147}Sm tends to exclude the effect of ionizing radiation in the pathogenesis of lung fibrosis. The concentrations of RE in lungs of heavy smokers were also compared with a group of non-smokers.

The high accumulation of rare earths in lungs and lymph nodes and the lung fibrosis of the worker examined indicates a possible long-term risk of rare-earth pneumoconiosis in occupational workers.

The relationship between the obvious accumulation of rare earths in human lungs under chronic exposure and the interstitial pneumoconiosis calls attention to proposals for MPC (maximum permissible concentration) limits of occupational exposure to rare earths in air in order to protect workers exposed to respirable rare-earth dusts.

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Antitumour Activity of Lanthanum

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Although the chemotherapy of malignant disease had its birth in the treatment of leukemia with potassium arsenite solution in 1865 by Lissaner, and although the majority of the elements of the periodic table are metals, the antitumour activity of inorganic substances has been little studied. Most antineoplastic agents are organic substances which are voluminous, less soluble in aqueous medium and have serious side effects. The only inorganic compound commonly used for some cancers is *cis*-dichlorodiamine platinum(II). Irreversible renal damage and ototoxicity are its serious drawbacks and limit the amount of the drug which can be administered. More recently antitumour activity of IIIA group metals has been examined [1] of which gallium(III) has emerged to possess the most potent antitumour activity. We have shown [2] that the free or loosely-bound gallium(III) is very effective in treatment of some experimental tumours in animals. Due to its high charge density (3.23) it is very difficult to get free or loosely-bound gallium(III) in solution and freshly prepared solutions had to be administered. This led us to study the antitumour activity of other trivalent elements. We took lanthanum as the first choice which has lower charge density (2.61) than that of gallium(III) and the biological properties of which has been extensively studied [3].

The antitumour activity of lanthanum was studied in Morris hepatoma-3924A-bearing rats. Solutions containing a single species of lanthanum(III) were administered. The purity and chemical nature of lanthanum(III) in aqueous solution was examined chromatographically and electrophoretically before its administration into the animals. Optimal dose of lanthanum was determined by administering different amounts of lanthanum solution in different group of animals of similar history. After the death of the animals the lanthanum in different organs and tumour was quantified by atomic absorption spectrometry and emission spectrometry. Our results have shown that lanthanum(III) is not a better antitumour agent than gallium(III) for Morris hepatoma-3924A. Antitumour activity for other types of tumours, e.g.,

Lewis lung tumour and mammary tumour, TGS, is under study.

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- 2 S. K. Shukla, I. Castelli, I. Blotta and S. Caroli, 'Gallium and Related Elements: Basic Science and Clinical Applications', *Int. Conf., Banff, Alberta, Canada*, 12–14 Sept. 1980, *Abstracts*, pp. 22–23.
- 3 G. B. Weiss, *Ann. Rev. Pharmacol.*, 14, 343 (1974).

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Extraction and Separation of Neptunium(IV), Plutonium(IV) and Americium(III) by Bidentate Organophosphorus Extractant

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This paper summarized the extraction and separation of Np(IV), Pu(IV) and Am(III) with dihexyl-N,N-diethyl carbamyl methylene phosphonate (DHDECMP)-diethyl benzene (DEB) in nitric acid medium.

The distribution ratio of Np(IV), Pu(IV) and Am(III) was studied as a function of a number of parameters such as concentration of nitric acid, salting-out reagents in the aqueous phase, contact time, and temperature. Stripping and separation of Np(IV), Pu(IV) and Am(III) from pregnant organic phase were studied. The suitable stripping and separation conditions were obtained. The enthalpy changes ΔH_{Np} , ΔH_{Pu} and ΔH_{Am} associated with their extraction process were estimated individually. The composition of extracted complex of Np(IV), Pu(IV) and Am(III) was determined.

Effect of Contact Time and Temperature. The experiment shows that equilibrium for all extracted species is reached in approximately 30 seconds of contact. The distribution ratios of Np(IV), Pu(IV) and Am(III) decrease with increase of temperature, while the effect of temperature on distribution ratio (D) of nitric acid is negligible. Consequently, the extraction process of the metallic ions is considered as an exothermic and it is not desired to increase temperature during extraction. In the plot of $\log D$ vs. $1/T(K)$ the straight lines were obtained. According to the slope of line and the Van't Hoff equation:

$$\Delta \lg D / \Delta (1/T) = -\Delta H / 2.303R,$$

the enthalpy changes ΔH associated with extraction process were estimated as follows:

$$\Delta H_{Np} \approx -3.7 \text{ Kcal/Mol}$$

$$\Delta H_{Pu} \approx -7.9 \text{ Kcal/Mol}$$

$$\Delta H_{Am} \approx -7.6 \text{ Kcal/Mol}$$

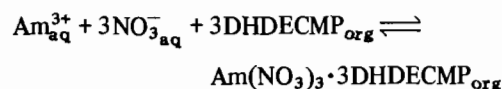
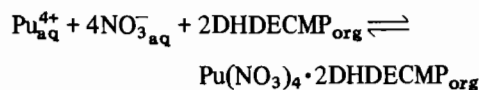
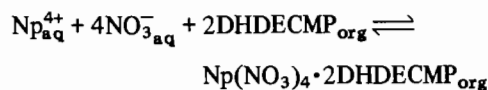
Effect of Concentration of Nitric Acid. The effect of nitric acid concentration in aqueous phase on extraction of trivalent and tetravalent actinides was investigated. The distribution ratios of Pu(IV), Np(IV) and Am(III) increase with concentration of nitric acid, so it is capable of extracting these actinides in higher concentration of HNO_3 . The data on the distribution ratios of these elements in 3 M HNO_3 medium are as follows:

$$D_{Np(IV)} = 221$$

$$D_{Pu(IV)} = 101$$

$$D_{Am(III)} = 2.2$$

Effect of Concentration of the Extractant. The distribution ratios (D) of these elements increase with DHDECMP concentration. The logarithmic plots of D_{Np} , D_{Pu} and D_{Am} versus DHDECMP concentration are straight lines with slopes of 2.0, 1.9 and 2.9 respectively. Therefore, the extraction reaction for Np(IV), Pu(IV) and Am(III) with DHDECMP can be expressed as:



Effect of Concentration of Salting-out Reagent. The experiment shows that the distribution ratios (D) of trivalent and tetravalent actinides increase obviously with concentration of $\text{Al}(\text{NO}_3)_3$ and NaNO_3 in aqueous phase. When the concentration of $\text{Al}(\text{NO}_3)_3$ is equal to 1.5 M in 3 M HNO_3 aqueous phase, the distribution ratios for Np(IV) and Am(III) are 1.15×10^3 and 10 respectively.

Back-Extraction. The stripping condition of Np, Pu and Am from the organic phase were investigated. It is shown that the Am(III) can be recovered quantitatively after twice stripping with 0.01 M HNO_3 . With (0.05–0.2 M) HNO_3 –0.05 M $\text{H}_2\text{C}_2\text{O}_4$ for Pu(IV), Np(IV) to be stripped or with (0.05–0.2 M) HNO_3 –0.05 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ for Pu(IV) to be stripped, the back-extraction percentage is more than 97 after twice contacts.