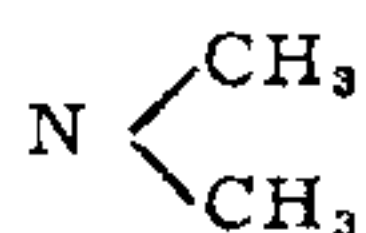
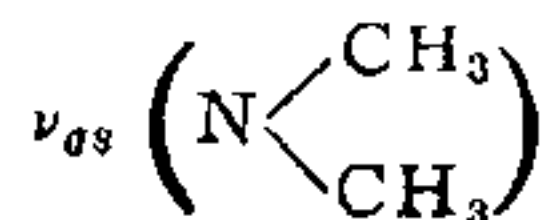


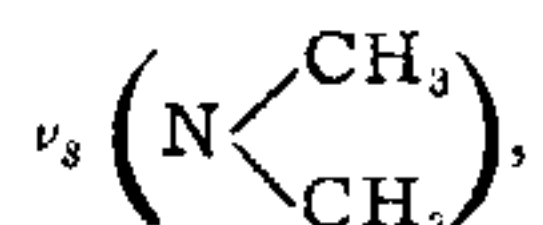
The bands at 1280 cm^{-1} and 760 cm^{-1} are due to the asymmetric and symmetric stretching vibrations of



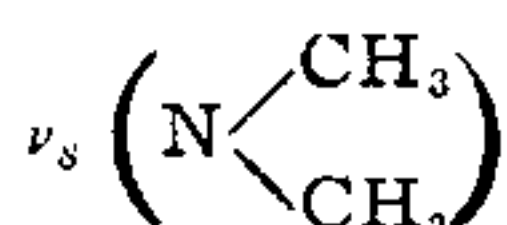
group. It can be seen from Table III that to the



mode of vibration,



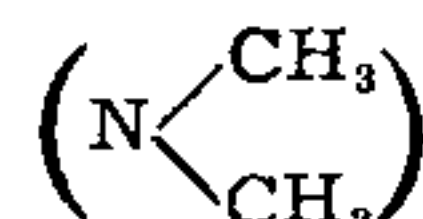
$\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{N})$ modes of vibrations contribute considerably. But for



only $\nu(\text{C}-\text{C}_2\text{H}_5)$ makes substantial contribution. The band at 1014 cm^{-1} is assigned to the $\nu(\text{C}-\text{C}_2\text{H}_5)$ and the potential energy distribution shows that the contribution from $(\text{N}-\text{CH}_3)$ stretching and $\delta(\text{O}=\text{C}-\text{N})$ bending vibrations to this mode are considerable. The bands at 1668 cm^{-1} and 1495 cm^{-1} are assigned to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{N})$ vibrations respectively

and there is considerable couplings between these two modes of vibrations. Similar results were obtained by Suzuki²⁻⁴ in case of acetamide and by the authors⁵ in case of N,N-dimethylformamide and N,N-dimethylacetamide.

The bands at 480 cm^{-1} , 243 cm^{-1} are assigned to the bending and rocking vibrations of



group and those at 395 cm^{-1} and 571 cm^{-1} to the rocking vibrations of $(\text{C}-\text{C}_2\text{H}_5)$ group and $(\text{O}=\text{C}-\text{N})$ bending vibrations respectively.

One of the authors (V. V. C.) is grateful to C.S.I.R., for the award of a Senior Research Fellowship.

1. Tatsuo Miyazawa, Takehiko Shimanouchi and Mizushima, S. I., *J. Chem. Phys.*, 1958, **24**, 408.
2. Isao Suzuki, *Bull. Chem. Soc. Japan*, 1960, **33**, 1360.
3. —, *Ibid.*, 1962, **35**, 540.
4. —, *Ibid.*, 1962, **35**, 1280.
5. Venkata Chalapathi, V. and Venkata Ramiah, K., *Proc. Ind. Acad. Sci.* (Under publication).
6. Venkata Ramiah, K., Venkata Chalapathi, V. and Indira Chai, C. A., *Curr. Sci.*, 1966, **35**, 350.

MICRODETERMINATION OF CERIUM IN MARINE ENVIRONMENT *

T. M. KRISHNAMOORTHY, V. N. SASTRY AND T. P. SARMA

Health Physics Division, Bhabha Atomic Research Centre, Bombay

THE distribution of trace elements between sea-water, sediments and biological species will aid in the understanding of the geochemical processes taking place in the sea. Since rare-earths belong to the group of elements dispersed in sea, the R.E. distributions together with other data is useful in the study of distribution of water masses in the oceans and in the solution of many geobiological problems. Due to the recent contamination of water masses by long-lived radioisotopes such as caesium-137, strontium-90 and cerium-144, etc., from bomb-explosions and discharges from nuclear installations, the study of rare-earths, especially cerium-144 distribution, is particularly important. Very little data are available of the distribution of R.E. in marine environment. The first measurements are that of Goldsmidt¹

and Balshov and Khitrov² on Indian Ocean waters. The procedure adopted by Balshov and Khitrov is for total rare-earth in sea-water samples only and there is a loss of about 5-25% of R.E. on activated charcoal. Goldberg³ determined the concentrations of the rare-earths in the Pacific Ocean Waters, Manganese nodules and Phosphorite samples by activation analysis. It is the objective of this investigation to develop a uniform colorimetric method for the estimation of cerium in all the three matrices of the marine environment, viz., sea-water, sediments and biological samples and to use this method for determining the cerium content in the marine environment off West Coast of India.

The sea-water and sediment samples are collected from Tarapur region (Latitude $19^\circ 45' \text{ N}$, Longitude $72^\circ 36' \text{ E}$) about 2-3 km. off-shore. Most of the biological samples are collected from nearby regions.

* This work is carried out under IAEA/BARC research Agreement No. 155/R3/CF.

About 60 litres of the sea-water samples are filtered through Whatman No. 42 filter-paper, acidified to a pH of about 2 with concentrated HCl. About 5 gm. of FeCl_3 is added and precipitated as hydroxide by adding ammonia to carry down rare-earths. The solution is filtered and the precipitate is dissolved in concentrated HCl. The iron solution along with rare-earths is passed through Dowex-1 anion exchange resin previously conditioned with 10 N HCl. Washing the column is continued with 10 N HCl. The effluent and the leaches which are free from iron are reduced to a small volume of about 50 ml. 5–10 mg. of calcium as carrier is added and precipitated as oxalate at pH 5 at two different temperatures which carries down rare-earth oxalates along with small amounts of manganese. In the final procedure 10 mg. of calcium is added and precipitated as oxalate at room temperature (28–30° C.). The oxalate precipitate is filtered through Whatman No. 42 filter-paper and the precipitate is ignited at 600° C. for about 3–4 hours to decompose the oxalate. In order to remove manganese, the residue is dissolved in 2 N H_2SO_4 and oxidised with potassium periodate to convert manganese to permanganate. 10 mg. of zirconium is added to the solution and zirconium precipitated as zirconium iodate. The effect of manganese decontamination is studied by taking 1 mg. of manganese and 10 mg. of zirconium and precipitating as zirconium iodate. The iodate precipitate is centrifuged and decomposed with H_2SO_3 and then taken up in 8 ml. of 1 N H_2SO_4 . 1 ml. of potassium persulphate solution (25 mg.) and 1 ml. of AgNO_3 (0.5 mg.) are added and the solution gently boiled for about 5 minutes to oxidise cerous to ceric. The volume is made up to 10 ml. and its absorbance is measured at 350 $m\mu$ and also at 520 $m\mu$ to correct for traces of manganese accompanying cerium. 30 litres of artificial sea-water is spiked with 100 μg . of cerium and the overall recovery of cerium by the above procedure is done in 2 samples and found to be about 75%.

The biological samples are ashed at 500° C. and the ash is digested with dilute HCl and centrifuged. The supernatant liquid is passed through Dowex-1 anion exchange resin as above and the further steps are followed as before.

Sediment samples are dried at 100–110° C. A known weight of the dried sample is leached

with N/20 HCl, 5% EDTA, 1 N ammonium citrate and 1 N ammonium acetate as described by Sarma *et al.*⁴ The leaches are evaporated to dryness, muffled at 500° C. and then taken up in concentrated HCl. Further steps are similar to that followed for sea-water.

20–100 μg . of cerium is taken and oxidised with potassium persulphate-silver catalyst and made up to 10 ml. The absorbances are measured at 320 and 350 $m\mu$ to get the calibration curves. The results are given in Fig. 1.

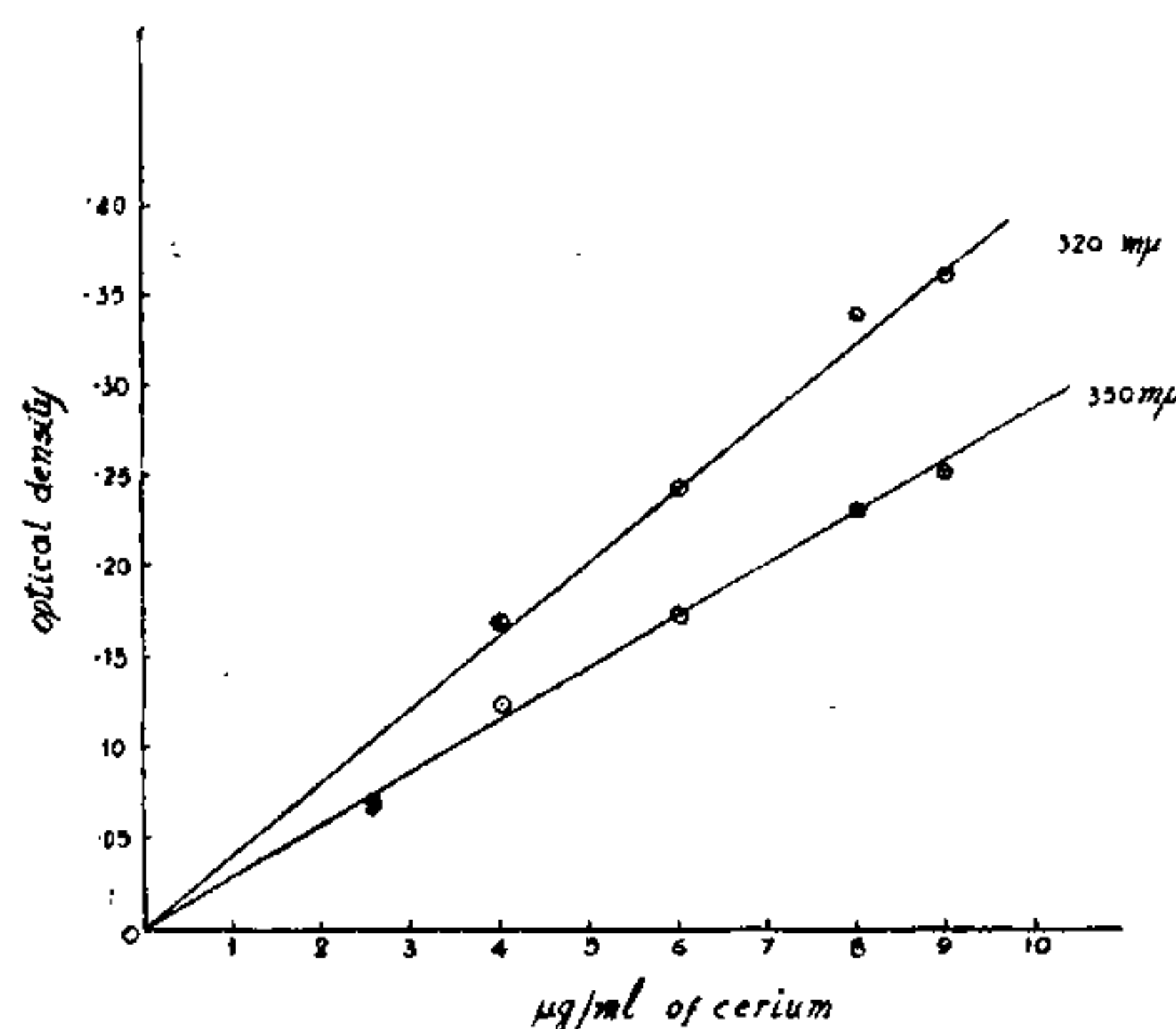


FIG. 1. Calibration curve for cerium.

Even though the sensitivity at 320 $m\mu$ is 0.025 $\mu\text{g}/\text{cm}^2$ for 1 cm. path length for $\log I_0/I = 0.001$, the actual measurements are made at 350 $m\mu$ with a sensitivity of 0.033 $\mu\text{g}/\text{cm}^2$ in order to avoid higher blanks. Interferences due to similar elements such as La and Th are studied and found to be negligible upto 0.1 mg./ml. The interference due to zirconium carrier used in the procedure is also found to be negligible.

Table I gives the effect of temperature and the carrier concentration in the co-precipitation of cerium with calcium oxalate. It is seen from Table I that higher temperatures inhibit the co-precipitation of cerium. The recoveries of cerium are good when 10 mg. of calcium carrier is added and the experiments are carried out at room temperature ($95 \pm 5\%$). Five blank experiments on the recovery of cerium on zirconium iodate in presence of 1 mg. of manganese have been carried out and they give a value of $95 \pm 5\%$ as shown in Table II.

The sediment and biological species contain varying amounts of manganese and even though 99% decontamination is achieved in the zirconium iodate precipitation step, it is necessary to correct for any accompanying trace amounts

TABLE I
Cerium co-precipitation with calcium oxalate

No.	Calcium carrier mg.	Temperature 28-30°C. absorbance of cerium		Cerium recovery %	Temperature 75-80°C. absorbance of cerium		Cerium recovery %
		Added OD	Obtained OD		Added OD	Obtained OD	
1	5	0.320	0.256	80	0.290	0.095	33
2	5	0.320	0.204	64	0.290	0.060	21
3	5	0.320	0.224	69
4	5	0.320	0.225	69
5	5	0.320	0.202	64
6	5	0.320	0.202	64
7	10	0.240	0.232	97	0.290	0.131	45
8	10	0.240	0.242	100	0.290	0.121	41
9	10	0.240	0.242	100
10	10	0.240	0.232	97
11	10	0.240	0.240	100
12	10	0.240	0.240	100
13	10	0.175	0.164	94
14	10	0.175	0.179	100
15	10	0.257	0.260	100
16	10	0.257	0.240	93

TABLE II
Decontamination of manganese in co-precipitation of cerium with zirconium iodate

No.	Test solution	Absorbance of cerium at 350 mμ			Accompanied manganese %	Cerium recovery %
		Added OD	Obtained OD	Net OD		
1	Reagent blank (Persulphate with Ag catalyst)	0.060
2	Reagent blank + 10 mg. Zn	0.060
3	Reagent blank + 10 mg. Zn + 1 mg. Mn	0.126	0.066	1.1	..
4	Reagent blank + 10 mg. Zn + 1 mg. Mn	0.130	0.070	1.2	..
5	Reagent blank + 10 mg. Zn + 1 mg. Mn	0.116	0.056	0.9	..
6	Reagent blank + 10 mg. Zn + cerium + 1 mg. Mn ..	0.160	0.270	0.150	1.1*	94
7	Reagent blank + 10 mg. Zn + cerium + 1 mg. Mn ..	0.160	0.270	0.150	1.1*	94
8	Reagent blank + 10 mg. Zn + cerium + 1 mg. Mn ..	0.175	0.290	0.170	1.1*	97
9	Reagent blank + 10 mg. Zn + cerium + 1 mg. Mn ..	0.175	0.295	0.175	1.1*	100
10	Reagent blank + 10 mg. Zn + cerium + 1 mg. Mn ..	0.175	0.292	0.172	1.1*	98

* The contribution of Mn in cerium absorbance is taken as 1.1%, average of test solution Nos. 3, 4 and 5.

of manganese (as permanganate) for absorbance of cerium wavelength, 350 mμ. In order to achieve this, manganese standards are prepared in the range of 1-5 μg./ml., oxidized with persulphate as earlier, and their absorbances are measured at 520 mμ and 350 m. These values are given in Fig. 2. The ratio of O.D. at 350 mμ to O.D. at 520 mμ is observed to be 0.5. In the actual samples, besides measuring the O.D. at 350 mμ for cerium, the measurements are also made at 520 mμ. From the absorbance obtained at 350 mμ, the contribution due to manganese is subtracted using the ratio from the graph.

In Table III are given the measured cerium content of sea-water, fishes and sediment leaches. The sea-water values obtained by us are agreeing with those obtained by Mauchline and Templeton⁵ and Balshov and Khitrov.² In the biological samples analysed (Pomfret, Ghol, Cat-fish, Lobster and Sea-hare), the accumulation factors vary from 200 to 450 whereas Mauchline and Templeton⁵ reported only a value of 12 for fishes. The HCl, EDTA and ammonium citrate leaches of sediments (average of 4 samples) are giving accumulation factors of about 20,000 whereas ammonium acetate leach is giving around 6000.

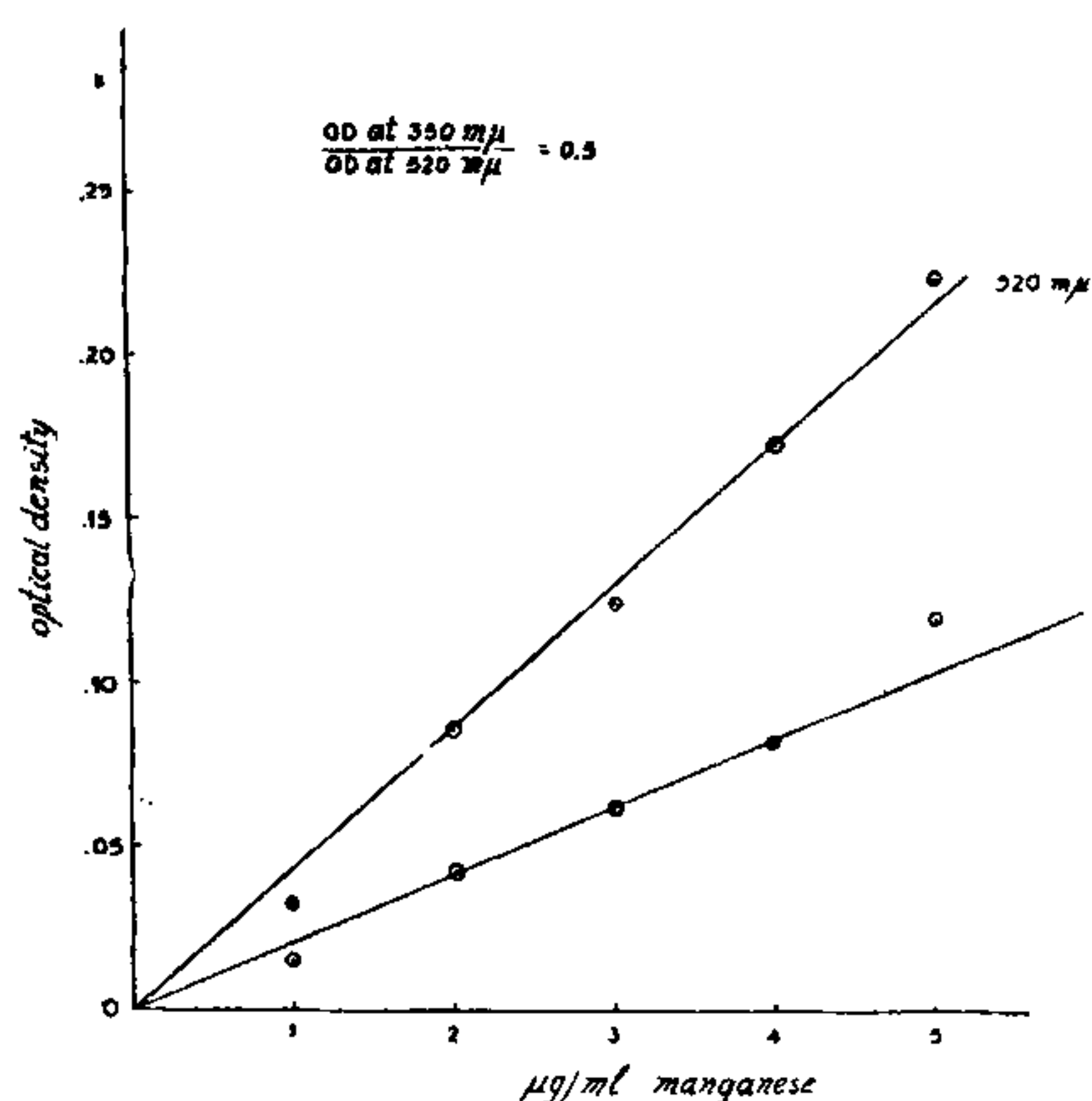


FIG. 2. Interference of manganese at 350 mμ.

TABLE III
Cerium content in different matrices of the
marine environment off Tarapur Coast

No.	Sample	Cerium content ppm
1	Sea-water	.. 1.0×10^{-3}
2	Sea-water	.. 0.8×10^{-3}
3	<i>Arius</i> sp. (Cat-fish)	.. 0.20
4	<i>Pseudosciaena dicanthus</i> (Ghol)	.. 0.38
5	<i>Pampus</i> sp. (Pomfret)	.. 0.38
6	<i>Panulirus polyphagus</i> (Lobster)	.. 0.32
7	<i>Aplysia</i> sp. (Sea-hare)	.. 0.40
8*	HCl leaches of sediment	.. 21.00
9*	EDTA leaches of sediment	.. 18.20
10*	Amm. cit. leaches of sediment	.. 21.00
11*	Amm. acet. leaches of sediment	.. 5.20

* Average of four samples. Biological samples are expressed on wet weight basis whereas sediment samples are expressed on dry weight basis.

Some of the general conclusions that can be drawn out of this work are :

- (i) The biological species accumulate large amounts of cerium,
- (ii) there is a large amount of labile cerium associated with sediments, and
- (iii) since EDTA and ammonium citrate are known to form strong complexes with rare-earths, similar values obtained for HCl, EDTA and ammonium citrate leaches is understandable.

We wish to express our deep appreciation to Dr. A. K. Ganguly, Head, Health Physics Division, Bhabha Atomic Research Centre, for initiating the work and his continued interest.

1. Goldsmidt, V. M., "The principle of distribution of chemical elements in minerals and rocks," *J. Chem. Soc.*, 1937, p. 655.
2. Balshov, A. and Khitrov, L. M., "The distribution of rare-earths in the waters of Indian Ocean," *Geochemistry, Eng. Trans.*, 1961, 1, 877.
3. Goldberg, E. D. and Koide, M., "Rare-earth distribution in marine environment," *J. Geophys. Res.* 1963, 68, 4209.
4. Sarma, T. P., Doshi, G. R., Gogate, S. S., Krishnamoorthy, T. M., Neralla, V. R., Rama Rao, M., Rao, S. R., Sastry, V. N., Shah, S. M. and Unni, C. K., "Geochemical investigations off Tarapur Coast," *J. National Institute of Sciences*, 1968 (In press).
5. Mauchline, J. and Templeton, W. L., "Artificial and natural isotopes in the marine environment," *Oceanogr. mar. biol. Ann. Rev.*, 1964, 2, 229.

MORPHOLOGY OF THE SHAGGY GLANDS OF *CLEOME VISCOSA* L.

N. RAMAYYA AND M. GOPALACHARYULU

Plant Anatomy and Taxonomy Laboratory,
Department of Botany, Osmania University, Hyderabad-7, A.P.

THOUGH plant hairs are well known for their taxonomic importance, a sustained use of these structures at all taxonomic levels has so far not come into practice. This is due to the fact that neither do we have authentic information about the total number of their types nor distribution in the vascular plants. Resume of mature trichome types occurring in

the different dicot families and several monocot groups have been given by Solereder⁰ and others,^{1,2,10-12} but one doubts if these could be taken as such, for typification in trichomes, particularly in the shaggy hairs, without a knowledge of their ontogeny, is not feasible. In a series of papers,³⁻⁷ the first author has earlier dealt with the structure, development,