

MICRODETERMINATION OF ZIRCONIUM IN MARINE ENVIRONMENT*

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AS Cs-137, Sr-90, Ru-106, Ce-144 and Zr-95-Nb-95 are produced in high yields in fission and appear as contaminants in marine environment, it is necessary to know the fate of these nuclides so as to limit their discharges into the sea. Mauchline and Templeton¹ summarised the work done on the distribution of Zr in the various matrices of marine environment. Mauchline² has determined the Zr-95 activity in sea-water, algæ, fishes and invertebrates arising out of discharges from Windscale nuclear installations. It is generally believed that Zr is effectively removed from sea-water by adsorption on the surfaces of fine particles such as silt.² Foreman and Templeton³ studied the uptake of Zr-95 activity on *Prophyra* sp. (algæ) and using autoradiography technique, they concluded that Zr is taken up mostly by adsorption. Most of the work carried out so far is on the distribution of Zr-95 in the marine environment and the methods adopted are different for different matrices. It is the objective of this investigation to develop a uniform method for the estimation of Zr in the various matrices of marine environment, viz., sea-water, sediment and biological species.

Sea-water and sediment samples were collected from Tarapur region (Lat. 19° 45' N., Long. 72° 36' E.) about 2-3 Km. off-shore during 1966-67. Most of the biological samples were collected from nearby region except one sample, *Meretrix meretrix* from Ratnagiri region (Lat. 17° 00' N., Long. 73° 30' E.).

Sediment samples are dried at 105-110° C. A known amount of the dried sample is leached with N/20 HCl, 5% EDTA, 1N ammonium citrate and 1N ammonium acetate as described by Sarma et al.⁴ The leaches are evaporated to dryness and muffled at 500° C. to destroy the organic matter and then taken up in 10 N HCl. Biological samples are also dry-ashed at 500° C. and then taken up in 10 N HCl.

The acid-soluble part of the biological and sediment leaches are oxidised with 0.5 g. of KBrO₃ to convert Fe⁺⁺ to Fe⁺⁺⁺ and centrifuged to remove silica. The clear solution is

then passed through Dowex-1 anion exchange resin previously conditioned with 10 N HCl. 2-3 column volumes of 10 N HCl are used for washing the column. Elements such as Ca, Mg, Al, Th, etc., are not adsorbed on the column at this acidity. Zr is held on the column along with Fe⁺⁺, U⁺⁺, Cr⁺⁺, and small amounts of cobalt and titanium. The column is eluted with 6 N HCl to desorb Zr. Small amounts of Co and Ti also accompany the Zr fraction. Tests have been made on the recovery of Zr at 6 N and 4 N HCl concentration of the leach. Even though, the recovery of Zr at 4 N HCl concentration is close to 100%, elution with 6 N HCl is preferred (recovery 80-85%) in order to avoid the contamination from Co. The Zr fraction was evaporated to dryness, converted to nitrate by treating with conc. HNO₃ twice and evaporating to dryness. The residue is taken up with 50 ml. of 5 N HNO₃ and 10 mg. of cerium carrier (sulphate form) is added. Cerium was precipitated as ceric iodate by adding 50 ml. of 0.35 M potassium iodate. Experiments were carried out to see the co-precipitation of Zr on ceric iodate and found to be 80-85%. Care is taken to avoid even traces of chloride in the solution, as chloride ion reduces ceric to cerous. The iodate precipitate is kept for 2-3 hrs. and centrifuged. The precipitate is taken up in 10 ml. of 4 N HCl and evaporated to dryness. Decomposition of ceric iodate by HCl is continued till no iodine vapours appeared. The residue is taken up in 10 ml. of 4 N HCl and 2 ml. of 0.25% Alizarin Red-S (in aqueous form) is added. The solution is made slightly alkaline with dilute ammonia. After 2-3 minutes, dilute HCl is added drop by drop till it is neutral, followed by 1.75 ml. of conc. HCl and the volume is made up to 50 ml. (overall acidity 0.4 N). The absorbance of the Zr lake is measured at 560 mμ. Experiments have been carried out to see the overall recovery of Zr by the above procedure.

About 60 litres of sea-water is filtered through Whatman No. 42 filter-paper and the pH is adjusted to about 2 with HCl. About 0.5 g. of iron carrier is added and precipitated as hydroxide with ammonium hydroxide to carry down Zr. The hydroxide precipitate is

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dissolved in conc. HCl and the above procedure is followed. A known amount of Zr is added to 60 litres of artificial sea-water and the recovery of Zr by the above procedure is determined and found to be 25–30%.

As the recoveries were low, experiments were conducted to see the collecting efficiency of ferric hydroxide for Zr. 500 ml. of sea-water was spiked with Zr-95 and acidified with HCl to pH 2. 15 mg. of Fe^{+3} (as nitrate) was added and the hydroxide precipitated with ammonia. The precipitate was centrifuged and planchatted. It was counted for Zr-95 betas using an aluminum absorber of 27 mg./cm.² thickness to cut off Nb-95 betas. The standard and the sample were counted under identical geometry conditions. The collecting efficiency of ferric hydroxide for Zr is found to range from 60–70% even in small volumes of sea-water of 500 ml. (Table I).

TABLE I

Collecting efficiency of ferric hydroxide for zirconium

No.	Activity of Zr-95*		Recovery %
	added cpm	obtained cpm	
1	854	593	69.4
2	854	570	66.8
3	794	500	63.0
4	794	480	60.5
5	794	490	61.7

* Nb-95 betas were cut off by using 27 mg./cm.² Al absorber.

50–250 μg . of Zr is taken and the colour is developed with the aqueous form of Alizarin Red-S. The volume is made up to 50 ml. with an overall acidity of 0.4 N. The absorbances are measured at 520 $m\mu$ and 560 $m\mu$ and the calibration curves are given in Fig. 1. Actual measurement of the samples is done at 560 $m\mu$ even though the absorbance of Zr lake at 520 $m\mu$ is high, in order to avoid higher blanks. 10 mg. of cerium do not show any interference in the estimations of Zr and small amounts of Th present in the samples are completely removed in ion-exchange step.

50–250 μg . of Zr is added to a 50 ml. solution of Fe^{+3} (as chloride) containing 50 mg. of iron in 10 N HCl and taken through the entire procedure, given above, in order to see the overall recovery of Zr at various concentrations and these results are given in Table II. As seen from this table, the overall recovery of Zr is $60 \pm 5\%$. Better results are obtained if the

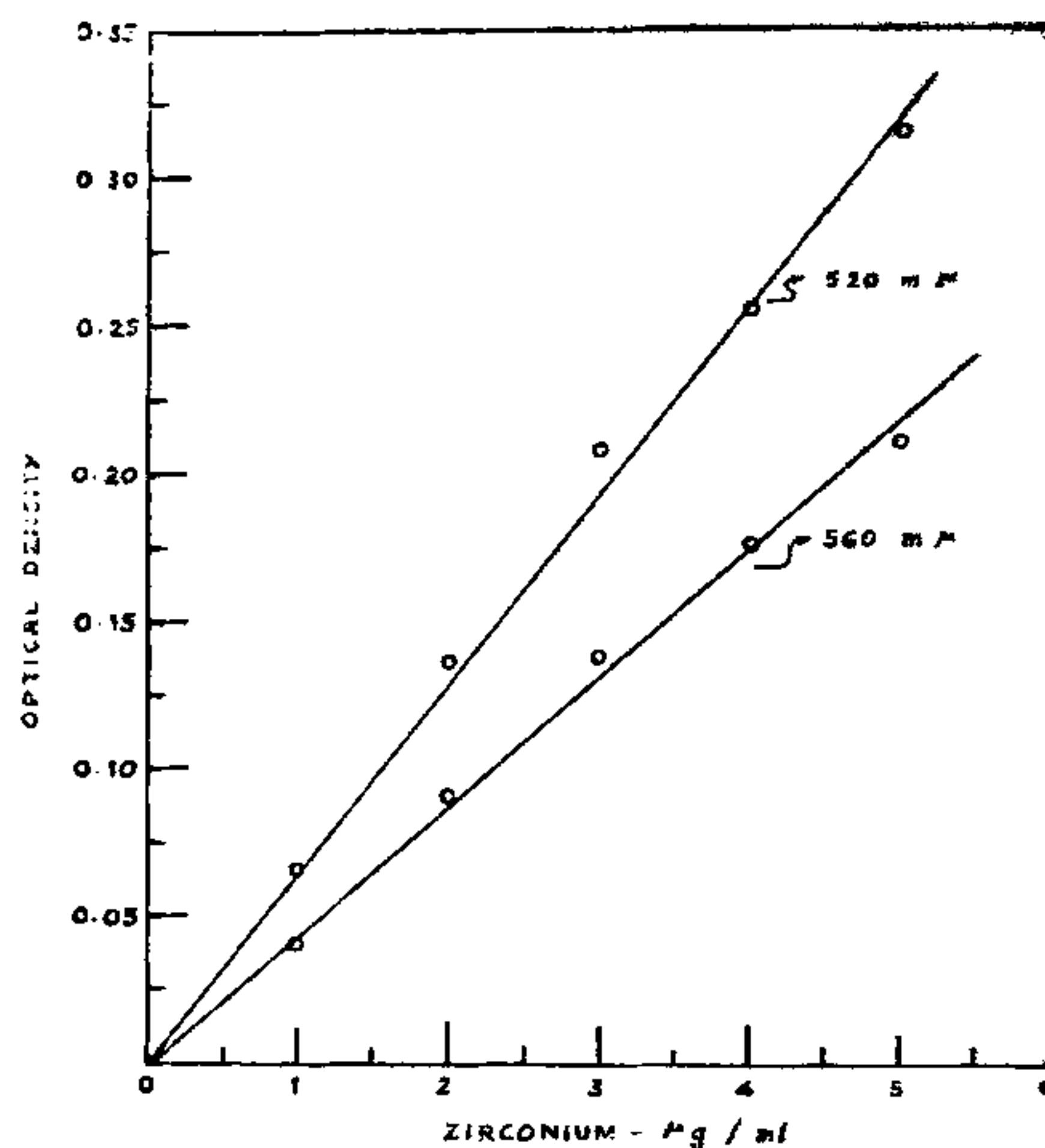


FIG. 1. Calibration of zirconium.

TABLE II

Recovery of zirconium at various concentrations

No.	Zirconium $\mu\text{g./m.}$	Optical Density		Recovery %
		added	obtained	
1	1	0.041	0.022	54
2	2	0.082	0.052	63
3	3	0.123	0.075	61
4	4	0.164	0.101	61
5	5	0.205	0.133	65

Zr concentrations is above 1 $\mu\text{g./ml}$. The results of analysis of sea-water, sediment and biological samples are given in Table III. Mauchline and Templeton¹ reported a value of 0.2 ppm. of Zr in sea-water whereas our values are in the range of 0.42×10^{-3} to 1.44×10^{-3} ppm. According to the above authors, most of Zr is in particulate form and they determined Zr in the total sea-water whereas we analysed in the filtered sea-water. There is also a significant difference between post-monsoon and pre-monsoon values. Out of the biological samples analysed, only *Aplysia* sp. (sea-hare) is showing a high enrichment factor of 700 whereas the fishes are showing around 80–150. The labile part of Zr in the various sediment leaches is very high (enrichment factor 2,500–16,000) as obtained from the various leach values. From the above observations, it appears that a good part of Zr entering the seas finds its way into the sediments rather than in the biological species.

TABLE III
Zirconium content in the various matrices of marine environment

No.	Sample		Location	Zirconium content ppm
1	Sea-water	..	Tarapur (Pre-monsoon)	1.44×10^{-3}
2	Sea-water	..	" (Post-monsoon)	0.44×10^{-3}
3	*HCl leach of sediment	..	" (Post-monsoon)	2.10
4	*EDTA leach of sediment	..	" (Post-monsoon)	7.88
5	*Amm. cit. leach of sediment	..	" (Post-monsoon)	2.73
6	*Amm. ac.t. leach of sediment	..	" (Post-monsoon)	1.21
7	<i>Aplysia</i> sp. (sea-narc)	..	" (Pre-monsoon)	1.17
8	<i>Pampus</i> sp. (pomlet)	..	" (Pre-monsoon)	0.14
9	<i>Otolithus brunneus</i> (Koth)	..	" (Post-monsoon)	0.06
10	<i>Meretrix meretrix</i> (Clam.)	..	Ratnagiri (Post-monsoon)	0.07

* Average of 4 sediment leaches. Values of biological samples are expressed on wet weight basis.

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THIRD INTERNATIONAL SYMPOSIUM ON EQUATORIAL AERONOMY

RECOGNISING the increasing activity of Indian scientists in the study of the earth's atmosphere and its environs, a number of working scientists in the fields of geomagnetism and aeronomy proposed that the Third Symposium on Equatorial Aeronomy be held in India. The first Symposium was held in Peru in 1962, and the second at Sao Paulo in Brazil in 1965.

The Department of Atomic Energy provided financial support to the Physical Research Laboratory (PRL) at Ahmedabad for conducting the symposium. Besides, Radio Science (URSI), the International Association of Geomagnetism and Aeronomy (IAGA) and the Inter-Union Commission of Solar Terrestrial Physics (ICUSTP) sponsored the symposium.

The symposium was held at Ahmedabad from the 3rd to the 8th February 1969. Nearly 70 scientists from nineteen foreign countries and 100 scientists from India participated in the symposium. Professor Sydney Chapman, the doyen of Aeronomy and Geomagnetism,

inaugurated the symposium and Dr. Vikram A. Sarabhai gave the welcome address.

The symposium discussed the following topics: The D-region at Low Latitudes; Ionospheric Absorption; Irregularities in the Equatorial Electrojet; Dynamo Currents and Electric Fields. The Neutral Atmosphere at Low Latitudes; Ionospheric Irregularities; Equatorial F-region; Total Electron Content; Air Glow; Neutral Particles and Ion-Chemistry; Dynamics of F-region; Ionospheric and Geomagnetic Tides; Magnetic and Ionospheric Storm-phenomena in the Equatorial Region; Exospheric Whistlers; Micropulsations; Magnetosphere and Solar-Terrestrial Relationships. Besides the formal sessions, there were many group discussions, informal discussions, lectures and visits.

An illustrated Abstracts will be published to bring together the main ideas and results exchanged during the course of the symposium.

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