yielded acetaldehyde DNPH (R_f 0·75) already described. The ether insoluble portion of DNPH (R_f 0·40) was first washed with a little alcohol to remove excess of reagent. The residue thus obtained crystallised from nitro-benzene as scarlet needles, .m.p. over 300°. (Found: C, 40·6; H, 2·7; N, 26·5; $C_{14}H_{10}N_8O_8$ requires C, 40·0; H, 2·3; N, 26·7.) Its identity as glyoxal DNPH was confirmed by comparison with an authentic sample using chromatography and I.R. spectrum. Glyoxal required for comparison was prepared by the hydrolysis of dichloro dioxane.[5]

Bisulphite extraction was also possible. A sample of the oil was dissolved in ether and extracted with a saturated solution of sodium bisulphite repeatedly. The bisulphite extract was decomposed with hydrochloric acid and treated with alc. HCl solution of 2,4-dinitrophenyl hydrazine. The product could be fractionated in the same way as mentioned above and all the three DNPH's were obtained. The residual ether solution on evaporation yielded the oil free from odour.

In continuation of the above work we had occasion to test a few other minor oils. Pongamia oil has also smell though it is not so unpleasant as that of nahor seed oil. In this case also steam distillation and bisulphite extraction removed the carbonyl compounds and they have been identified as acetone and glyoxal. Essential details are given below :

Pongamia oil was subjected to steam distillation and DNPH was collected as described in the case of nahor oil. It was fractionated into ether soluble and ether insoluble portions. The former was passed through a column of silica gel and crystallised from alcohol; m.p. 121–23°. Its identity as acetone DNPH was confirmed by comparison with an authentic sample using co-chromatography and m.m.p. The ether insoluble portion of DNPH was washed with a little alcohol and crystallised from nitrobenzene yielding scarlet needles, m.p. over 300°; $\lambda_{m\cdot x.}$ 580 mμ in aq. methanolic potash.[4] (Found C, 40·4; H, 2·8; N, 27·0; $C_{14}H_{10}N_8O_8$ requires C, 40·0; H, 2·3; N, 26·7.) Its identity as glyoxal DNPH was confirmed by comparison with an authentic sample.[5]

Neem oil is notorious for its markedly unpleasant odour. Steam distillation however removes most of the odour. The DNPH from the oil steam distillate was collected as in the above cases, and fractionated into ether soluble and ether insoluble portions. The former was a mixture of 4 DNPH's which have not been identified ; but its spectrum is characteristic of mono-DNPH. The ether insoluble fraction after washing with a little alcohol was repeatedly crystallised from nitrobenzene. It was identical with the DNPH of glyoxal obtained from nahor oil and also synthetically prepared.[5] In the bisulphite extract of the oil only glyoxal could be obtained.

1. Salway, A. H., *J. Chem. Soc.*, 1917, **111**, 407.
2. Allen, R. K., *Chem. and Ind.*, 1965, p. 1560.
3. Gehrig, R. F. and Knight, S. G., *Appl. Microbiol.*, 1963, **11**, 166.
4. Wells, C. F., *Tetrahedron*, 1966, **22**, 2685.
5. Böeseken, Tellegen and Henriques, *Proc. Roy. Soc. Amsterdam*, 1931, **34**, 631.

URANIUM DISEQUILIBRIUM IN ARABIAN SEA

T. P. SARMA AND T. M. KRISHNAMOORTHY

Health Physics Division, Bhabha Atomic Research Centre, Bombay

SINCE the discovery of high U^{234}/U^{238} activity ratios in natural waters percolating through uranium ore beds by Russian workers,[1] the attention of many scientists[2-5] has been directed towards the disequilibrium studies of uranium in other natrual materials. The disequilibrium of uranium in nature is significant since this anomaly may be used as a geochemical tool in the study of rocks, soils and natural waters. The first encouraging results of Thurber,[2] on Einwetok corals which gave a value of 1·17 ± 0·03 for the U^{234}/U^{238} activity ratio, accelerated the work by other workers[6-8] in looking for uranium isotopic composition in sea-waters, shells and marine carbonates. Most of the sea-water studies are confined to the Pacific and the Atlantic Oceans and the accepted value for these waters is 1·15 ± 0·02. Recently Veeh[9] has determined the U^{234}/U^{238} ratio in Red Sea and reported also the same value. There is no data on Indian Ocean waters, especially on coastal waters. It is the objective

of the present investigation to determine the uranium isotopic ratio in waters, quite near the coast, off West Coast of India, and to see whether any difference exists between these values and those obtained by other workers in the open and coastal waters.

Four sea-water samples, about 40 litres each (1 mile off shore), are collected along with two shell samples from the beach of Tarapur. The sea-water samples are filtered through Whatman No. 42 into polyethylene carboys and about 150 ml. of concentrated HCl is added while stirring and kept for 2 hours. 500 mg. of iron solution is added and precipitated as hydroxide to carry down uranium. The solution is filtered and the precipitate preserved. On determining the uranium fluorimetrically in the hydroxide precipitate and the original sea-water, it has been found that only 40–50% of the total uranium is carried along with a single hydroxide precipitate. In order to get higher recovery values the above procedure is repeated three more times adding 500 mg. of iron each time. The hydroxide precipitates are mixed and dissolved in dilute nitric acid and boiled for sufficient time to precipitate silica. The solution is cooled and silica is removed by centrifugation. The clear solution is oxidised with potassium bromate and reduced in volume to 30–40 ml. and acidity adjusted to 1 N. About 40–50 gm. of solid aluminium nitrate (1 gm. per ml. of solution) is added and uranium extracted with an equal volume of ethyl acetate (BDH A.R.). The organic phase containing uranium is destroyed with concentrated nitric acid and evaporated to dryness. The residue is taken up in 8 N HCl and passed through Dowex 1 anion exchange resin which was previously conditioned with 8 N HCl. The column is thoroughly washed with 8 N HCl and uranium along with Fe^{III} and traces of Pa^V and Po^{VI} is leached with 0·5 N HCl. The leach solution is evaporated to dryness and dissolved in 20 ml. of 6–8 N HCl. The solution is extracted with an equal volume of methyl iso-butyl ketone (BDH A.R.) when Fe^{III}, Pa^V and Po^{VI} are extracted into organic phase leaving behind uranium in the aqueous phase. The aqueous phase is separated and the organic layer is back-extracted 4 more times with 6 N HCl to remove uranium completely. The aqueous phase and the back extracts are mixed and evaporated to dryness. The residue is radiochemically pure uranium. The shell samples are dissolved in ammonium acetate-acetic acid buffer of pH 5, filtered and

the filtrate is subjected to the above purification steps.

The residue is taken up in 5 ml. of 0·5 N nitric acid and transferred into a 1″ diameter electroplating unit. 5 ml. of saturated ammonium oxalate is added. The cathode is a 1″ diameter stainless steel disc (buffed). The anode is a platinum guaze. A current of 1–1·5 amp. is passed for about 2 hours. The stainless steel disc containing uranium is then warmed over a flame for about 5 to 10 minutes to remove traces of organic matter. The sample is counted with ORTEC 1 cm. surface barrier detector, coupled to a ORTEC low noise pre-amplifier unit. The spectra is recorded in a Nuclear data 512 channel analyser.

The overall chemical recovery of the procedure is tested for three samples using 20 gm. calcium carbonate (free from uranium) and adding known amounts of uranium. The recoveries are 90 ± 5%. The plating efficiency is separately determined using standards and it is found to be almost 100% within statistical errors when above-mentioned conditions are satisfied. The total uranium content of the samples is separately estimated by fluorimetric analysis.

The location of the water and shell samples analysed are given in Table I along with uranium isotopic ratios. As seen from Table I, the U^{234}/U^{238} ratio from Bombay and Tarapur sea-waters are giving values close to 1·16 ± 0·03, whereas the shell samples are giving slightly different values of 1·20 ± 0·03 and 1·11 ± 0·04. In Figs. 1, 2 and 3 are given the alpha spectra of two of the water samples analysed along with a standard uranium sample for comparison. Uranium standard (Fig. 3) shows two distinct peaks of U^{235} whereas the spectra of the samples show no such distinction.

Even though the water samples are from coastal region, the observed average value of 1·16 ± 0·03 is not different from open ocean values as reported in the literature for the Pacific and Atlantic Oceans. This suggests that the input of uranium from land drainage into coastal waters is not significant to affect any isotopic differences between coastal and open ocean waters. Large differences in the isotopic ratios of uranium in other natural waters have been reported in the literature[1,10] and the observed variations in the U^{234}/U^{238} ratios in the shell samples can be largely attributed to the environmental changes in

2

TABLE I

U^{234}/U^{238} activity ratios in sea-water and shells

| No.	Sample	Location		Date of collection		Uranium content ppm	U^{234}/U^{238}
		Lat. °N	Long. °E				
SW-1	Sea water ..	19° 48′	72° 38′ (Tarapur)	October	1966	$2 \cdot 7 \times 10^{-3}$	$1 \cdot 15 \pm 0 \cdot 02$
SW-2	do. ..	19° 48′	72° 38′ (Tarapur)	November	1967	$2 \cdot 7 \times 10^{-3}$	$1 \cdot 17 \pm 0 \cdot 03$
SW-3	do.	18° 50′	72° 35′ (Bombay)	April	1968	$3 \cdot 0 \times 10^{-3}$	$1 \cdot 18 \pm 0 \cdot 04$
SW-4	do.	18° 50′	72° 45′ (Bombay)	June	1968	$3 \cdot 0 \times 10^{-3}$	$1 \cdot 15 \pm 0 \cdot 03$
SH-1	*Astrea semicostata* sp. (shell)	19° 48′	72° 38′ (Tarapur)	October	1967	$0 \cdot 34$	$1 \cdot 20 \pm 0 \cdot 02$
SH-2	*Nerita* sp. (shell) ..	19° 48′	72° 38′ (Tarapur)	October	1967	$0 \cdot 14$	$1 \cdot 11 \pm 0 \cdot 04$
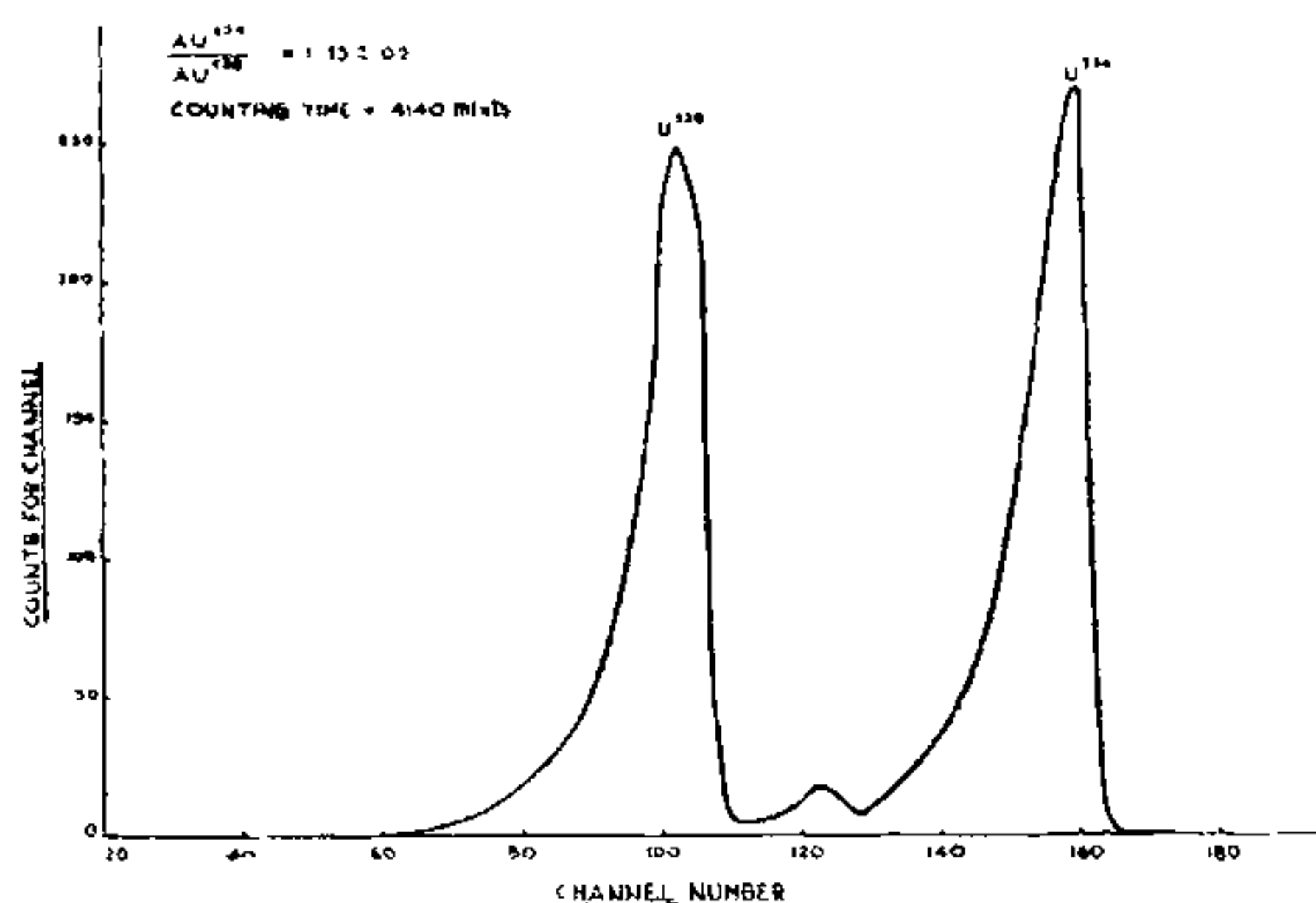
FIG. 1 Sea-water from Tarapur (SW-1).
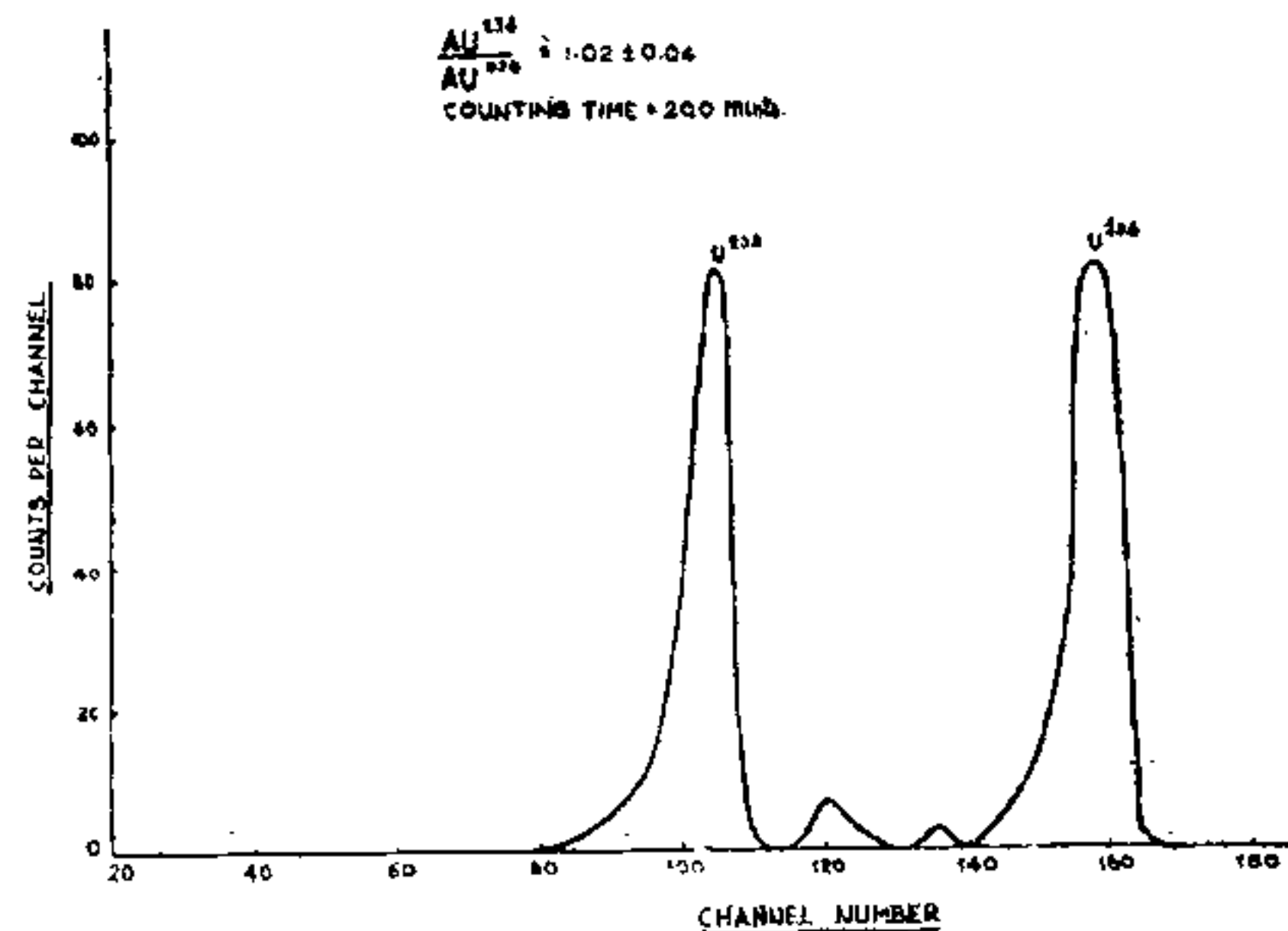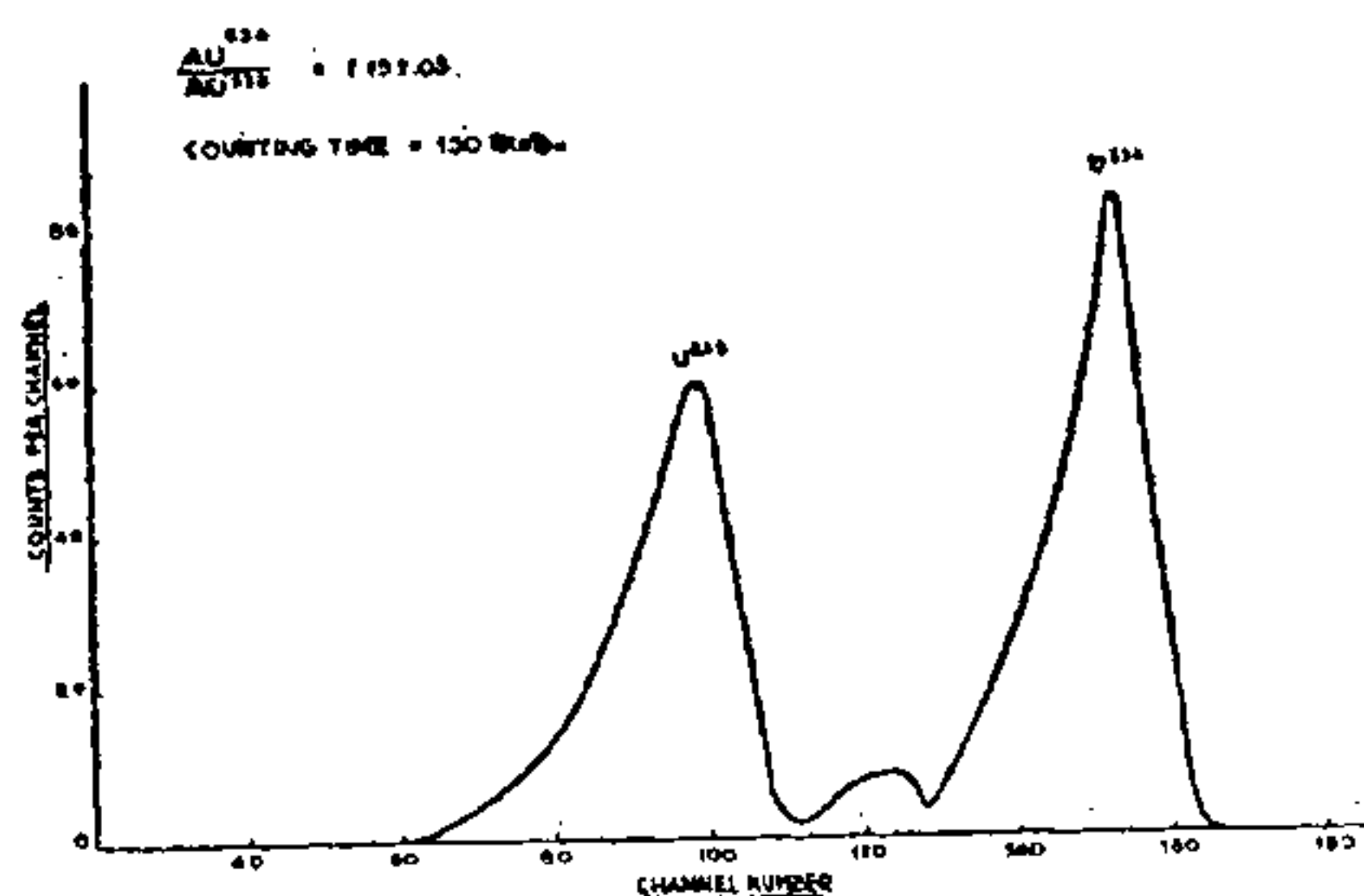

FIG. 2 Sea-water from Bombay Harbour (SW-4)

which they are grown. The observed disequilibrium of uranium in the shells and sea-water open up the possibility of determining the sedimentation rate in coastal regions which contain high calcium carbonate along with a good amount of shell material.

FIG. 3. Uranium standard.

We wish to express our appreciation to Dr. A. K. Ganguly, Head, Health Physics Division, Bhabha Atomic Research Centre, for the encouragement given to us during the investigation.

1. Isabaev, E. A., Usatov, E. P. and Cherdyntsev, V. V., *Radiokhimi*, 1960, **2**, 94.
2. Thurber, D. L , *Jour. Geophy Res.*, 1962, **67**, 4518.
3. Moore, W. S. and Sackett, W. M., *Ibid.*, 1964, **69**, 5401.
4. Teh-lung Ku, *Ibid.*, 1965, **70**, 3457.
5. Blanchard, R. L., Cheng, M. H. and Potratz, H. A., *Ibid.*, 1967, **72**, 4745.
6. Broecker, W. S. and Thurber, D. L , *Science*, 1965, **149**, 58.
7. Koide, M. and Goldberg, E. D., *Progress in Oceanography*, Pergamon Press, New York, 1965, **3**, 173.
8. Veeh, H. H., *Jour. Geophy. Res.*, 1966, **71**, 3379.
9. —, *Geochim. Cosmochim. Acta*, 1968 **32**, 117.
10. Blanchard, R. L., *Jour. Geophy. Res.*, 1965, **70**, 4055.