

Short notes

Mercury in the Atlantic around Iceland

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The recognition of the hazards to ecology, and even to human life, arising from the discharge of effluents containing mercury has led to considerable interest in the occurrence of the element in the aquatic environment. As would be anticipated, most research has been directed towards environments, such as lakes and estuaries, which are at greatest risk from dangerous pollution because of restricted exchange of water. Only comparatively little information is available about the concentration of the element in neritic waters (see, *e.g.* Stock and Cucuel, 1934; Burton and Leatherland, 1971; Topping and Pirie, 1972; Gardner and Riley, 1973). For ocean waters a limited amount of data is available for mercury distribution in the Pacific (Hosohara, 1961; Hamaguchi, 1961; Weiss, et al., 1972), North East Atlantic (Burton et al., 1971), the Greenland Sea (Carr et al., 1972) and the surface waters of the Atlantic and Indian Oceans (Chester et al., 1973). This paper presents data for the distribution of mercury in the water column in the North Atlantic around Iceland.

Samples were collected in a National Institute of Oceanography polypropylene water sampling bottle. Immediately after collection they were transferred unfiltered to acid-washed, silicone treated, 2.5 l glass bottles and acidified to pH 1.8 by addition of 40 ml of 9 N sulphuric acid which had been purified by extraction with a 0.05% solution of dithizone in carbon tetrachloride. Tests showed that sea water samples could be stored in this way for at least 6 weeks with no significant loss of mercury. Analysis of the samples was carried out at Liverpool using a combination of dithizone extraction and cold vapour atomic absorption spectrophotometry. Although the method used resembles that employed by Chau and Saitoh (1970) for the analysis of lake waters, there are several important differences, and for this reason it is described below.

Determination of mercury in sea water

Atomic absorption spectrophotometry was carried out by means of a Techtron AA5 instrument equipped with a hollow cathode mercury lamp and digital read-out. A 10 cm fused silica cell was used for absorption measurements.

Reagents

Water to be used in the analysis was purified by redistilling it through an all-glass apparatus and then passing it through a column of the hydrogen form of the cation exchanger (*e. g.* Dowex AG50 WX8). *Dithizone solution (0.005%)*. 25 mg of dithizone was dissolved in 500 ml of redistilled carbon tetrachloride. The solution was stored in a dark glass bottle in a refrigerator. If necessary it was purified by extraction with 6 M hydrochloric acid and then washed with water. When highly polluted waters are to be analyzed it is advisable to use 0.05% dithizone solution to ensure complete extraction of mercury.

Sodium nitrite solution 10% w/v

Hydroxylamine hydrochloride solution 20% w/v

Hydrochloric acid 5 M. Purified by passage through a 60 cm × 1.1 cm² column of Deacidite FF anion exchanger.

Stannous chloride reagent 30%. Stannous chloride dihydrate was dissolved in 30 ml of purified 5 N hydrochloric acid and diluted to 50 ml with water. The reagent was purified by bubbling nitrogen through it for a few minutes. This reagent soon became oxidized and was prepared afresh every day.

Procedure

An aliquot (2.03 l) of the acidified sample was transferred to an acid-washed 2 l separating funnel and extracted with two 15 ml aliquots of dithizone (shak-

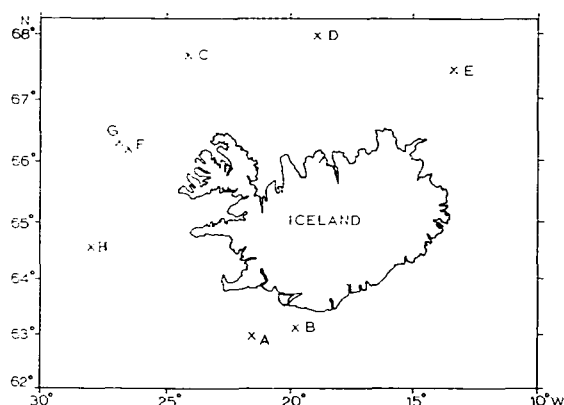


Figure 1. Locations of sampling stations.

ing mechanically for 5 min. in each instance). The extracts were combined in a 50 ml separating funnel and treated with 15 ml of 5 M hydrochloric acid. Sodium nitrite solution (0.5 ml) was added to decompose the dithizone and the separating funnel was shaken mechanically for 5 min. to revert mercury to the aqueous phase. After separation of the aqueous phase, the carbon tetrachloride layer was washed with 5 ml of water. The back extract and washings were combined in a 25 ml stoppered measuring cylinder. Nitrite was reduced by the addition of 1 ml of hydroxylamine hydrochloride solution and the solution was diluted to 25 ml with water. After not less than 30 min. 1 ml of stannous chloride solution was added and a bubbling head was fitted to the cylinder immediately. Air was then circulated at a rate of 130 ml min⁻¹ through a closed circuit consisting of a peristaltic pump, the measuring cylinder containing the solution, a short drying tube filled with magnesium perchlorate and the 10 cm cell of the atomic absorption spectrophotometer. A steady absorbance at 253.7 nm was attained after < 30 sec. This was maintained for about 90 s, after which a slow fall set in. To determine the reagent blank 2 l aliquots of acidified sea water were stripped of mercury by extracting them twice with 15 ml portions of dithizone, 40 ml of 5 N sulphuric acid was then added and the determination was continued as described above. The blank normally corresponded to about 7 ng Hg l⁻¹. Standards were run in a similar fashion, except that the stripped sea water was spiked with 100 or 200 ng of mercury (added as acidified mercuric chloride solution). The calibration curve was found to be linear up to 500 ng of mercury.

The precision of the method was assessed by carrying out 6 replicate analyses on a sample of water from the Irish Sea. These gave an average mercury content of 50 ng l⁻¹ with a coefficient of variation of $\pm 2.5\%$. The recovery of mercury by this proce-

dure was checked by performing duplicate analyses on 2 l aliquots of dithizone-extracted sea water after spiking them with 50–200 ng of mercury; these gave recoveries of mercury of between 97 and 99%. The optical density increments / ng of mercury obtained in this way lay within $99 \pm 2\%$ of those obtained when known amounts of mercury were added directly to the measuring cylinders in the final stage of the analysis. Tests showed that methyl mercury was also quantitatively determined during the analysis.

Results and discussion

Sampling was carried out at the 9 stations around Iceland indicated in Figure 1. The results of the analyses of unfiltered samples are presented in Table 1. The general range of mercury concentrations is similar to that found by Carr et al., (1972) for the Greenland Sea, and, if a few unusually high values are excluded, to that found by Burton et al., (1971) for the North East Atlantic. There are several water masses present in the area being examined. An attempt was made to determine whether these water masses are characterized by particular mercury concentrations. For this purpose, the water masses from which the samples were drawn were identified using the T-S criteria suggested by Stefansson (1962). The data in Table 1 provide little evidence for a correlation of mercury concentration with particular water masses. However, the few results available suggest that the mercury concentration is high in samples of the low salinity Polar Water which enters the Iceland Sea from the north. This is in agreement with the reports by Carr et al., (1972) of high mercury levels in a more northerly part of this water mass, the southward flowing East Greenland Current. These workers suggested that melting sea ice may have contributed some of this mercury to the water and they have pointed out that Weiss et al., (1971) have reported high concentrations of the element in glacial ice from Greenland.

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Table 1. Mercury concentrations in North Atlantic water from around Iceland (25 May–6 June 1972) and water masses

Map Code	Station No.	Lat. and Long.	Total depth (m)	Water mass	Sampling depth (m)	Temp. (°C)	Salinity (‰)	Mercury concentration ng l ⁻¹
A	B7/72-5	63°00'N 21°28'W	1010	Atlantic	0	8.24	35.16	98
				Atlantic	200	7.85	35.18	58
				Atlantic	600	6.49	35.12	78
				Atlantic	1000	5.12	35.05	225
B	B7/72-6	63°07'N 19°54'W	1100	Atlantic	0	8.60	35.20	28
				Atlantic	200	8.02	35.16	147
				Atlantic	600	7.30	35.17	16
				Atlantic	1000	5.20	35.05	72
C	B7/72-52	67°43'N 24°03'W	1280	Polar	0	-1.28	33.42	208
				Polar	200	0.26	34.72	118
				Arctic Intermediate	800	0.06	34.91	85
				Arctic Bottom	1270	-0.74	34.88	58
D	B7/72-67 & B2/72-106	68°00'N 18°50'W	1050	Arctic	0	3.04	34.70	115
				Arctic	100	-0.05	34.74	27
				Arctic Intermediate	200	0.66	34.89	27
				Arctic Intermediate	290	1.13	34.96	26
				Arctic Bottom	600	-0.14	34.90	50
				Arctic Bottom	963	-0.66	34.92	29
				Arctic Bottom	1000	-0.70	34.90	28
E	B2/72-63	67°30'N 13°20'W	1770	Arctic	0	-0.58	34.77	-
				Arctic	100	-0.42	34.81	38
				Arctic Bottom	978	-0.72	34.92	53
				Arctic Bottom	1580	-0.91	34.92	221
F	B2/72-127	66°15'N 26°30'W	618	Arctic Intermediate	354	0.81	34.85	43
				Arctic Intermediate	610	0.07	34.95	72
G	B2/72-128	66°20'N 26°48'W	516	Polar	0	-0.18	34.46	63
				Arctic	140	0.47	34.75	26
H	B2/72-129	64°37'N 28°00'W	1010	Atlantic	0	6.66	35.08	40
				Atlantic	200	6.63	35.09	12
				Atlantic	500	6.16	35.06	28
				Atlantic	1000	4.27	35.01	54

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