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ORGANOTIN COMPOUNNDS IN THE SOUTH COAST OF TURKEY (NORTHEASTERN MEDITERRANEAN)

Introduction:

FAO/UNEP/IAEA/WHO *ad hoc* meeting on organotin compounds (Athens, 5-7 October 1987) reviewed the global information on the tributyltin (TBT) and its derivatives in the marine environment. The group recommended that a pilot monitoring study in Mediterranean could be organized. Among the others, southern coast of Turkey, because of hot-spot sites, was chosen as a pilot area. METU-Institude of Marine Sciences agreed to participate for monitoring of TBT and derivatives namely dibutyltin (DBT) and monobutyltin (MBT) in the southern coast of Turkey. Here the data obtained from the area studied (Figure 1) is presented.
The area includes parts of the Northern Levantine basin. The shelf area in the region extending from Marmaris to Mersin, is deep and narrow. The shelf widens in the region lying between Mersin and Iskenderun. Off Iskenderun, Ceyhan, Seyhan and Berdan rivers together with other streams have built a shelf zone of 70 km wide which is most important part of the Northeastern Mediterranean in terms of biological life. The physical oceanography of the region has been studied relatively extensively and physical parameters responsible for the transport and dispersion of pollutants in the marine environment have been summarized by UNIDATA (1986). The chemical and biological oceanography of the region have also been summarized recently by Salihoğlu *et al.* (1987) and Bingel (1987). It suffices here to say that the nutrient levels are low as is the case for the Mediterranean at large. The biological life is rather patchy and is mostly found near the river mouths and limited upwelling areas. Description of the sampling stations is displayed in Table 1.

Results:

The butyltin results of this work are displayed in Table 2. As can be seen from the table, İskenderun Harbour contains TBT all the sampling period except July, 1988. The unexpectedly high quantities of MBT in İskenderun Harbour can be attributed to (1) either degradation of TBT after sampling (2) or the presence of a continious release of TBT to the harbour which leads to the accumulation of TBT.
It may be concluded that the high level of DBT in sea water is a proof of recent introduction of toxic TBT. In February, 1989 the high concentration of MBT in Mersin Harbour may be the result of the degradation of TBT introduced into the sea in late summer. A localized input of TBT, where boats are cleaned before repainting and old paint is removed in particulate form which can then contaminate sediment in that area, contaminated samples from a dry dock were sampled (Table 2).
It is seen from Table 2 that the ratis of TBT to the breakdown products are variable. This situation verify that TBT degradation in Mediterranean

occurs at different rates depending on the environmental factors.
The results of this survey strongly support the fact that at this moment Mediterranean ecosystem could be endangered by the use of TBT as antifoulant. Because the short residence time of TBT in sea water alone is not an adequate criterion to evaluate its potential envirnmental. Considering its propensity for uptake by plant material researchers must also establish the pathway for TBT transfer within the food chain.
Representative sediment samples from heavily contaminated harbours and estuaries were investigated. The observed organotin species are mono-, di-, tri- methyltins and monobutyltin. Existance of di- and tri- butyltin compounds in these samples is a question mark. Since the method used for sediment analysis is not applicable for the formation of di- and tributyltin hydrides even for the spiked sediment samples. On the other hand, the method used by Dahab (1989) was also tried but di- and tributyltin could not be observed.
No butyltins were observed in water samples taken from BOTAŞ during November sampling period. The odor of the samples and the visual inspection indicate that the samles were contaminated with crude oil. The formation of butyltin hydrides could be inhibited by hydrocarbons.

Experimental:

The sea water samples of the surface layer for the butyltin analysis were obtained (from upwind of the ship or by a rubber boat to be sure that the water samples were not contaminated by the ship) in 2 liters volume of glass bottles with teflon lined screw-caps and acidified with 2 ml of acetic acid. Samples were stored at 4° till analysis. For the analyses hydride derivatization atomic absorption method (HDAA) used.
Briefly after equilibrating the samples to room temperature 400 ml aliquat was placed in a reaction vessel and 3 ml of 4% $NaBH_4$ was injected for hydridization. The hydrides generated were purged with helium and trapped at liquid nitrogen temperature in a V-shaped glass column packed with 3% OV-1 coated Chromosorb-W. The collected hydrides were volatilised into the quartz furnace using a heating mantle.
The apparatus set up is shown in Figure 2 and the typical chromotograms are illustrated in Figure 3.

TABLE 1 DESCRIPTION OF THE SAMPLING STATIONS
(For station locations refer to Figure 1)

STATION NO	CHARACTERISTICS
A3	İskenderun Harbour; the harbour is located in a semienclosed bay which receives discharges from industry (agrichemical, foodagri, petrochemical, textile and iron-steel) and occupied by commercial ships. Also within the bay there is a oil terminal (BOTAŞ) which is the outlet for the pipeline from Qirkug oilfield of Iraq. The bay is known to be one of the rare fertile patch of the Mediterranean. It is estimated that almost 50 % of shrimp stocks of Turkish Mediterranean coast is in the bay.
A1ß	Mersin Harbour; this is located in a bay with good water exchange. This bay receives domestic and industrial discharges Dry docks within the harbour are one of the possible source of TBT. The harbour is busy and used by commercial ships (4550 commercial ships/year) including oil tankers, fishing boats and pleasure craft.
A21	Antalya Marina; this small marina is usually occupied by pleasure and small fishing boats (excluding trawlers).
A30	Marmaris Marina; this marina is an enclosed estuary and is occupied almost completely by pleasure boats. Maintenance of the boats is carried out within the marina.
REFERENCE STATIONS	These stations were chosen to confirm that inputs of TBT other than shipping activity unlikely to occur. Harbour and marinas were selected to demonstrate that environmental problems with TBT.

TABLE 2 CONCENTRATIONS OF ORGANOTINS IN NORTHEASTERN COASTAL WATERS (As butyltin chloride, ng/l), (Station locations are shown in Figure 1)

SAMPLING SITE	SAMPLING STATION	SAMPLING DATE	MBT	DBT	TBT
İskenderun		May, 1988	8	56	83
Bay	A3	July, 1988	2774	484	nd
		Nov., 1988	8	23	31
		Feb., 1989	27	7	32
Botaş	A35	May, 1988	140	nd	91
İşdemir	A4	May, 1988	21	15	nd
Marmaris	A30	May, 1988	nd	121	11
		July, 1988	nd	742	353
		Dec., 1988	60	7	33
Mersin Bay	A13	May, 1988	30	266	935
Antalya Bay	A21	May, 1988	nd	677	154
Mersin Bay Drydock		Nov., 1988	84	133	59
Reference	A78	July, 1988	nd	nd	nd
Stations	A65	Oct., 1988	nd	nd	nd

nd: Not detectable (below the detection limit of the applied method)

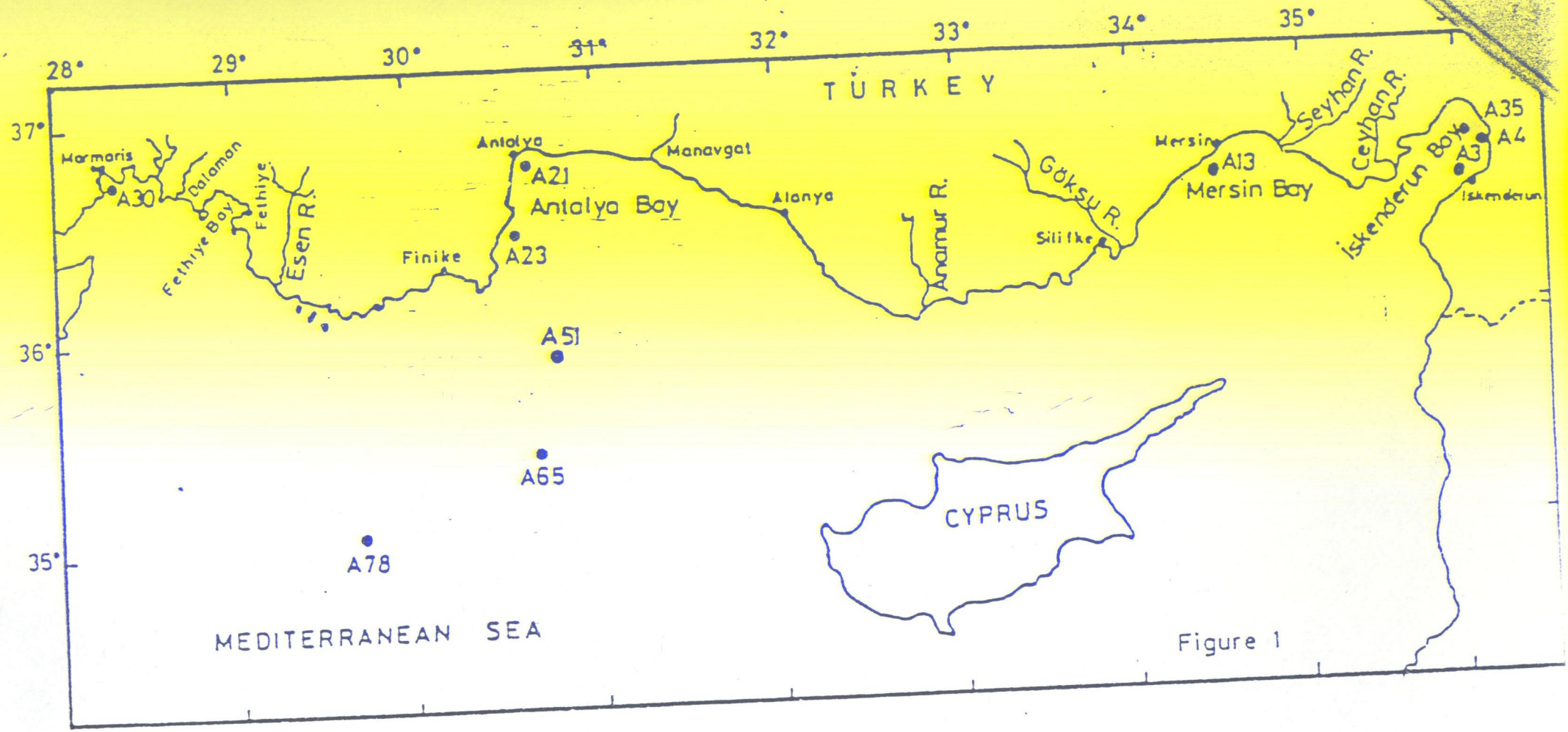
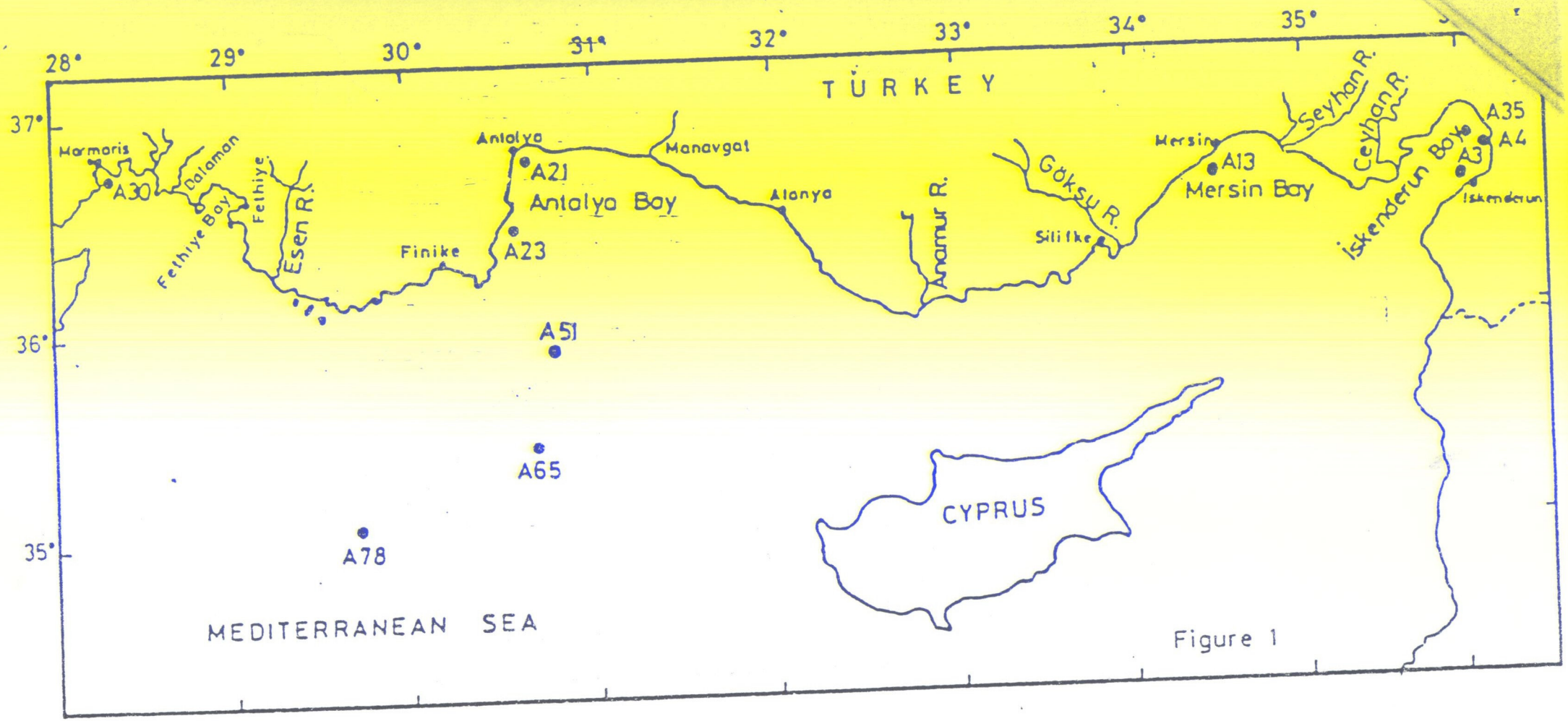

28°
29°
30°
31°
32°
33°
34°
35°
37°
36°
35°
TÜRKEY
Marmaris
A30
Dalaman
Fethiye Bay
Fethiye
Esen R.
Finike
Antalya
A21
Antalya Bay
A23
Manavgat
Alanya
Anamur R.
Göksu R.
Silifke
Mersin
A13
Mersin Bay
Seyhan R.
Ceyhan R.
İskenderun Bay
A35
A4
A3
İskenderun
A51
A65
A78
CYPRUS
MEDITERRANEAN SEA

Figure 1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Alanya
Anamur R.
Göksu R.
Silifke
Mersin
A13
Mersin Bay
Seyhan R.
Ceyhan R.
İskenderun Bay
A35
A4
A3
İskenderun
A51
A65
A78
CYPRUS
MEDITERRANEAN SEA

Figure 1

Figure 3 Typical chromatograms of;
a. Standards; TBT 200 ng, DBT 50 ng, MBT 20 ng
b Sea water sample from Mersin Harbour

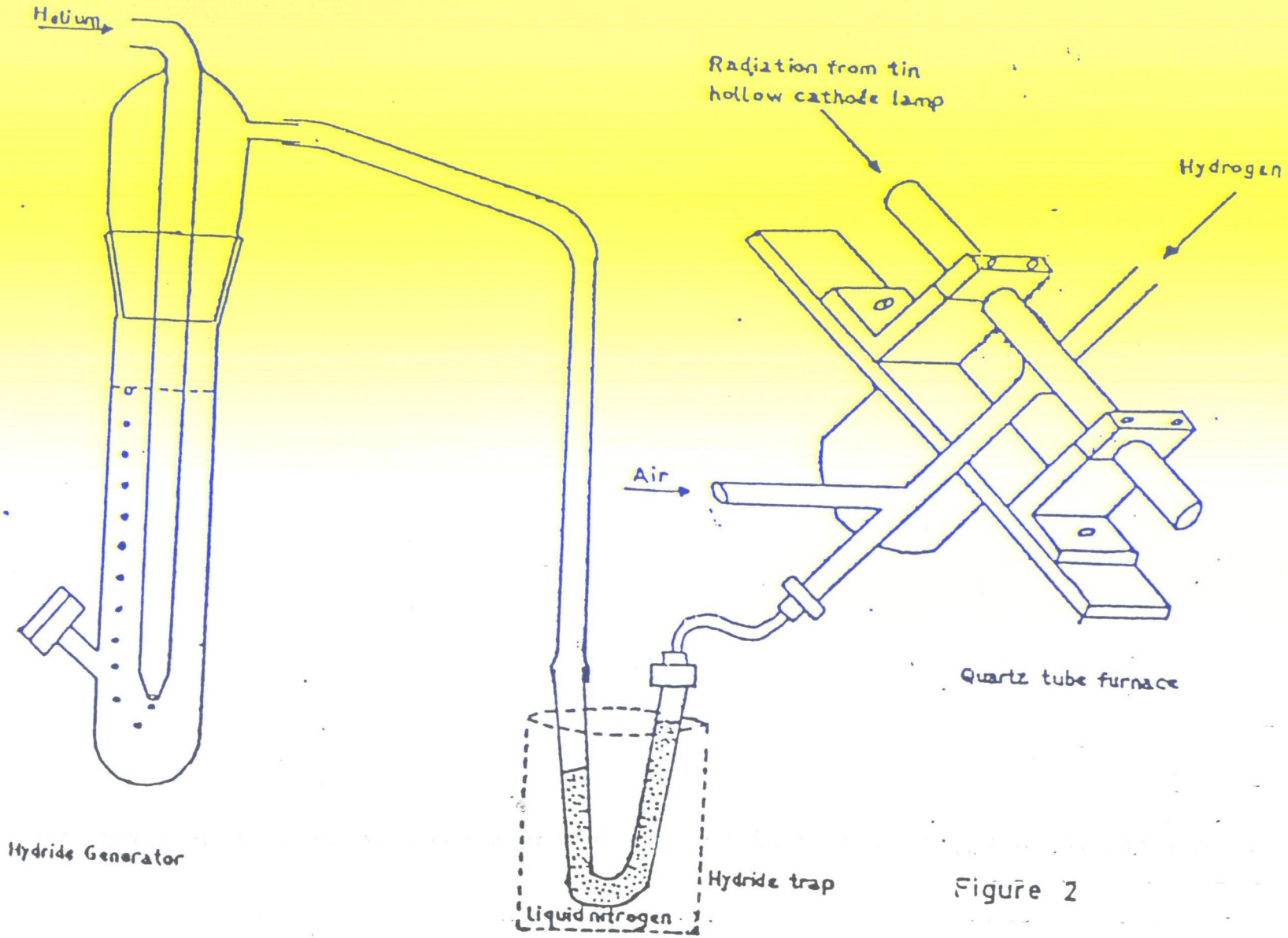
Helium
Radiation from tin hollow cathode lamp
Hydrogen
Air
Quartz tube furnace
Hydride Generator
Hydride trap
Liquid nitrogen

Figure 2