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STUDY OF TRACE ELEMENTS IN STRATIFIED WATERS OF THE TYRRHENIAN SEA FROM THE SURFACE TO 1.000 METERS DEPTH (*)

BY

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(Avec 7 dépliants)

I. ABSTRACT

During the last 10 years, the Sub-Committeee on Oceanographic Research of NATO has realized many expeditions in the Tyrrhenian Sea and has allowed us to study its hydrology, surface currents, bathymetry and gravimetry.

By its topography and characteristics (especially by its deep waters of very long residence time) we have identified it to a close basin. Indeed there are not any important coming waters from the rivers, and the surface currents let us see waters coming out between Sicily and France and in the Strait of Messina; in the other hand two parallele volcanic ridges, one of them being submarine, give an important amount of elements and oligo-elements.

We are studying trace elements in stratified waters from the surface to 1.000 meters depth and we hope of going on with the series of cards previously done.

This work is a complete description and an objective critic of sampling technics and the neutronic activation analysis.

Comparing the first results of Tyrrhenian waters with those of the Gulf of Tarente in which we have not any important amounts, we have given a first interpretation. The quantitative analysis of Co, Rb, Fe, Sc and Zn

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will be done by relative or absolute method. A list of all elements found by neutronic activation analysis will be detailed for each analysed sample.

II. INTRODUCTION

For more than 10 years the NATO Subcommittee on Oceanographic Research has organized many expeditions with the collaboration of French, Italian, Greek, Turkish and Belgian oceanographic ships.

These different expeditions have allowed us to study deeply the Mediterranean Sea and mainly the fundamental problems of physical oceanography.

We have especially studied : the currentometry (Technical Report 42), the hydrology (Technical Report 44) and the bathymetry (MORELLI, 1970) in the Tyrrhenian Sea. Following these different fundamental data we are going to know that the Tyrrhenian basin is pratically closed; its hydrographic system is without importance. Anyway we have mentioned coming waters into the Sicialian channel and, on the North, between the Corsican Cape and Genova. The deep Tyrrhenian basin is thus a stratified basin of Mediterranean water with a long residence time.

The most important source of trace elements are the submarine volcanic sources.

Two aims are studied here :

1) Refering to the previous works and obtained data (1), (2), (3), (4) we shall try to show up the volcanic inputs in this basin at the level of trace elements in stratified Mediterranean waters;
2) We shall determine the amount of Sc, Co, Rb, Zn, Fe.

We will try to determinate these amounts with maximum precision by the absolute method.

Anyway we have to consider errors and interference effects of first and second order due to the method, in other words to the neutronic activation.

III. EXPERIMENTS

1. Choice of stations

Sampling was done during the cruise organized by the Sub-Committee on Oceanographic Research of NATO in June 1969 on the Italian ship the « Bannock » from the « Consiglio Nazionale delle Ricerche ».

We fixed the stations referring to the submarine topography in other words in the depth, far from canyons to avoid the influence of the currents of convection along the sides as well as upwelling currents.

Fig. 5 shows the different points we choiced :

Point 1	39°14'	N	12°24'	E
Point 2	39°15'	N	17°57'	E
Point 3	40°21'	N	17°13'	E
Point 4	40°25'3"	N	17°08'	E
Point 5	40°02'30"	N	10°32'	E
Point 6	38°26'08"	N	15°04'9"	E

At the first and the fifth stations in the Tyrrhenian Sea sampling has been done until 1.000 meters depth, every 200 meters. Besides one sample has been taken above and under the thermoclyne.

Station 2 in the Gulf of Tarente will be comparated with the other station. Indeed the Gulf of Tarente is quite different from the Tyrrhenian Sea : for instance, there is none volcanic input but well an important hydrographic system and an important exchange with the other waters.

2. Sampling

The sampling technique and the preparation of the samples before and after the irradiation are described in the NATO Technical Report (5).

2 cc of sea water of each sample have been irradiated in quartz phials in the following conditions :

Nuclear Center of Saclay (C. E. A.).
Irradiation time : 5 days.
Thermic neutron flux : $\varnothing_r$: 2.5×10^{12} n/sec/cm^2 (at 2,200 m/sec).
Resonance neutron flux : $\varnothing_r$: not knowned.
Fast neutron flux : $\varnothing_f$
$\varnothing_r / \varnothing_{th}$: $1/10^2$.

After the irradiation, the quartz phial can be only opened after 8 days cooling to let decrease the activity of Na^{24}. Afterwards the activated water is poured into sealed perspex containers.

Each sample is three times quantitatively and qualitatively analysed :

- the first time, one week after the irradiation so that Na and Br can be analysed in order to fix the flux (the Na can be also analysed by atomic absorption);
- the second time, one month after the end of the irradiation, to analyse elements of middle and long lifes;
- the third time, two months after the irradiation to analyse elements of long half-life.

3. Quantitative analysis

Two methods allowed us to determine the amounts of the elements present in the sample before irradiation :

1) one is the **relative method** : we irradiate simultaneously the complex sample (containing an unknown weight of the element to be determined) and a standard (a well-known weight) of the same element.

The induced activity during the irradiation is proportional to the weight of the elements contained in the original sample.

2) The other one is the **absolute method** : these is possible when the induced activity is linked to the amount of elements present, by the equation :

$$A_B = N_A \left[g \, \varnothing_{th} \, \sigma_0 + (0.45 \, \sigma_0 + I) \, \varnothing_r \right] \left[1 - e^{(-\lambda_B t)} \right] \qquad (I)$$

for the reaction A (n, γ) B

In the reaction (I) we have :

A_B : activity of the radioisotope B at the end of the irradiation
$\varnothing_{th}$: thermic neutron flux (velocity of 2,200 m/sec)
$\varnothing_r$: resonance neutron flux
σ_0 : cross section of the reaction (at 2,200 m/sec)
I : resonance integral
g : correctif factor necessary if the cross sections does not follow a 1/v law in the thermic region (v represent the neutron speed)
λ_B : disintegration probability of the radioisotope
t : irradiation time
N_A : number of atoms of the element A.

The advantage of the second method is in the fact that it is not necessary to irradiate an important number of standards, and specially in the case of the study of oligo-elements in sea water.

The inconvenient is that we see in the relation (2) that fundamental factors appear such as the flux, the cross-sections and the resonance integral. These factors are sometimes not very precisely known.

We have used the second method to estimate and to reduce the errors.

Unfortunately the nuclear center of Saclay could not mention exactly the ratio of the resonance flux to the thermal flux. Therefore we calculated the specific activity and the quantity of elements for different ratios : 1/30, 1/20 and 1/10, the most probable value being between 1/10 and 1/20.

4. Errors

We can notice that the precision of a quantitative analysis depends of :

- a precise knowledge of the cross-section and the integrate of resonance;
- the precision of the flux;
- the precision in measuring the activity.

5. Induced error on quantitative analysis by absolute method

The differential calculation of the relation (I) gives us the absolute error.

Error on the flux. — We already know that the flux of neutrons varies with the position of the sample during the irradiation; the measured variations can reach 11 % but no more.

Error on the cross-section and on the integral of resonance. — These errors are different for each element : therefore the absolute method needs elements with precise knowing cross-section.

Error on the activity. — It depends of the statistic error due to the disintegration and, on the other hand, on the error on air evaluation. This error is less than 4 % if we are working in good conditions : long counting rates and wide surface of photopeak.

This is an idea of extrinsic errors too; indeed we expressed hypotheses to be able to apply the formula of quantitative analysis by the absolute method.

6. Results

Table 1. Specific activities of Sc, Fe, Co, Rb and Zn.
Table 2. Quantitative analysis of Sc, Fe, Co, Rb, Zn in sea water, in ppb.
Table 3. Position and depth of the samples.

7. Figures

The figures 1 to 4 represent the different cruises of the ships with the Belgian participation at the International expedition in the Tyrrhenian Sea for the following measurements :

1) GEK and surface temperature.
2) Instantaneous values of surface currents in the Tyrrhenian Sea.
3) Instantaneous values of surface currents in the Straits between Sicily, Tunis and Italy.
4) GEK surface currents in the Tyrrhenian Sea.

TABLE 1.

Specific activities of Sc, Fe, Co, Zn and Rb (in d. p. m/gr)

	σ_o (barn)	I (barn)	$\frac{\varnothing r}{\varnothing_{th}} = 0$	$\frac{\varnothing r}{\varnothing_{th}} = \frac{1}{30}$	$\frac{\varnothing r}{\varnothing_{th}} = \frac{1}{20}$	$\frac{\varnothing r}{\varnothing_{th}} = \frac{1}{10}$
$A_{46_{\mathrm{Sc}}}$	22 ± 2	10.2	1.78×10^{12}	1.83×10^{12}	1.86×10^{12}	1.94×10^{12}
$A_{59_{\mathrm{Fe}}}$	0.98 ± 0.1	0.58 ± 0.16	3.564×10^{8}	3.688×10^{8}	3.75×10^{8}	3.936×10^{8}
$A_{60_{\mathrm{Co}}}$	36.3 ± 1.5	55.2 ± 4.5	1.001×10^{11}	1.067×10^{11}	1.1×10^{11}	1.198×10^{11}
$A_{65_{\mathrm{Zn}}}$	0.44 ± 0.05	0.67 ± 0.14	4.101×10^{9}	4.38×10^{9}	4.496×10^{9}	4.891×10^{9}
$A_{87_{\mathrm{Rb}}}$	0.80 ± 0.08	9. ± 2.8	1.098×10^{10}	1.527×10^{10}	1.741×10^{10}	2.384×10^{10}

TABLE 2

Amounts (in p. p. b.) of Sc, Fe, Co, Zn and Rb in the different samples.

	Elements														
	Sc			Fe			Co			Zn			Rb		
$\varnothing_r/\varnothing_{th}$	1/30	1/20	1/10	1/30	1/20	1/10	1/30	1/20	1/10	1/30	1/20	1/20	1/30	1/20	1/10
Number sample															
060	0.0068	0.0067	0.0064	82.53	80.92	77.09	0.332	0.321	0.313	755.09	735.77	716.45	73.95	65.65	48.41
063	—	—	—	21.27	20.94	119.95	0.114	0.110	0.107	93.80	91.40	89	73.95	66.05	48.87
069	—	—	—	63.82	62.83	59.99	0.228	0.220	0.215	243.88	237.64	231.40	96.21	84.29	61.77
070	0.0487	0.0479	0.0459	26.11	25.70	24.49	0.104	0.101	0.098	43.15	42.04	40.94	62.47	54.09	40.11
071	0.0350	0.0345	0.0330	58.02	57.12	54.42	0.085	0.083	0.081	52.53	51.18	49.84	81.85	71.71	52.55
073	0.0341	0.0335	0.0321	29.01	28.56	27.21	0.095	0.092	0.090	51.59	50.27	48.95	79.70	69.82	51.17
074	0.0204	0.0201	0.0193	53.19	52.36	49.89	0.218	0.211	0.206	93.80	91.4	89	89.03	78.00	57.16
075	0.0165	0.0163	0.0156	26.11	25.70	24.49	0.948	0.092	0.090	51.59	50.27	48.95	81.85	71.71	52.55
078	0.0399	0.0392	0.0376	31.91	31.42	29.93	0.284	0.275	0.269	168.84	164.52	160.20	75.39	66.05	48.87
079	0.0341	0.0335	0.0321	101.54	99.96	95.24	0.616	0.596	0.582	1782.20	1736.60	1691.0	73.24	64.16	47.02
080	0.0088	0.0086	0.0083	35.78	35.22	33.59	0.171	0.165	0.161	150.08	146.24	142.40	73.24	54.09	47.02
081	0.0126	0.0124	0.0119	26.11	25.70	24.49	0.218	0.211	0.206	136.01	138.53	129.05	62.47	60.38	40.11
082	0.0078	0.0076	0.0073	44.48	43.79	41.72	0.161	0.165	0.161	136.01	132.53	129.05	68.93	54.09	44.26

TABLE 3

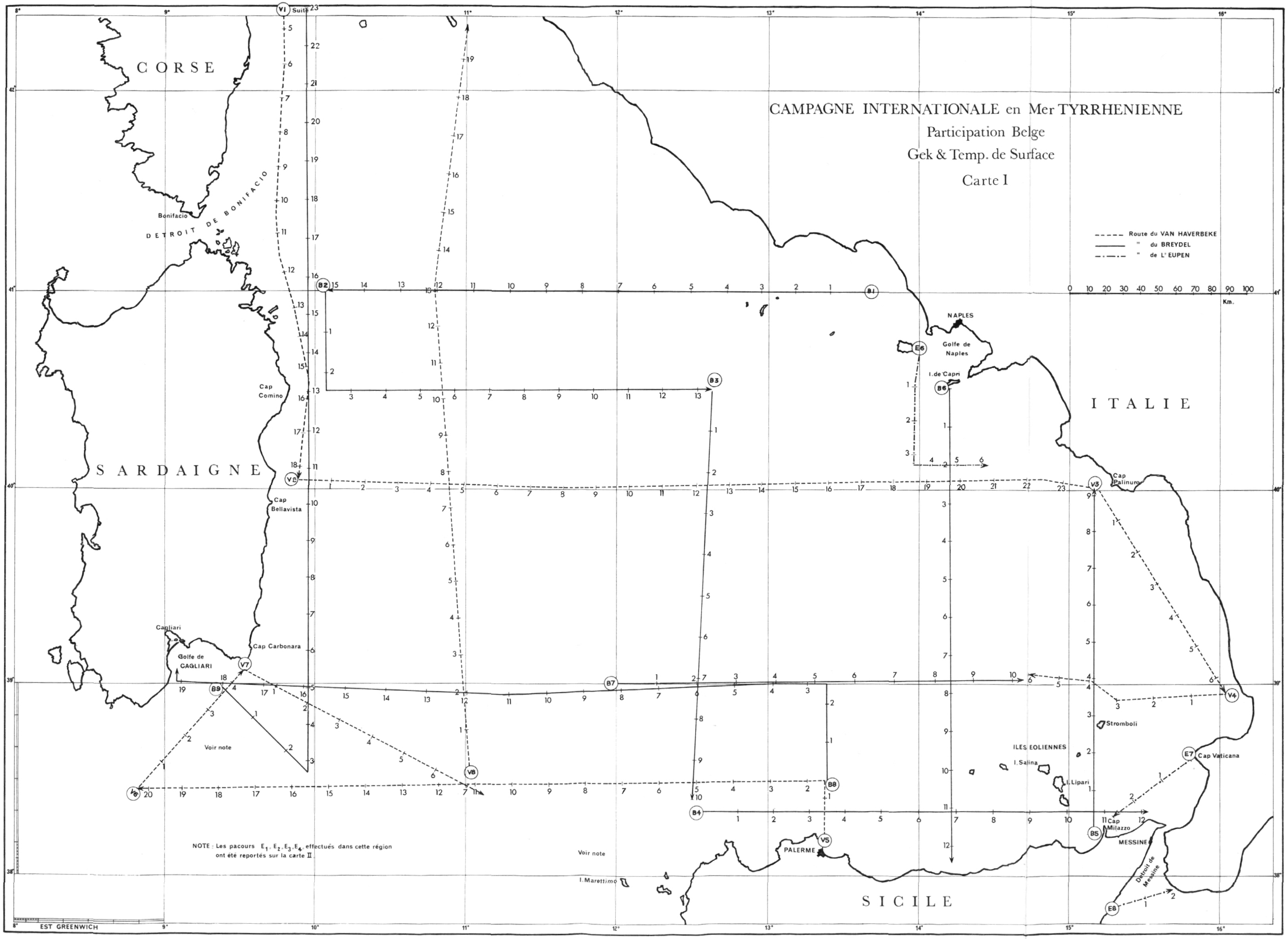
Position and depth of the stations

Sample number	Depth (in m)	Position	
060	40	39°14' N	12°24' E
063	195	39°14' N	12°24' E
069	50	39°15' N	17°57' E
070	100	39°15' N	17°57' E
071	150	39°15' N	17°57' E
073	400	39°15' N	17°57' E
074	600	39°15' N	17°57' E
075	800	39°15' N	17°57' E
078	100	40°02' N	13°32' E
079	100	40°02' N	13°32' E
080	600	40°02' N	13°32' E
081	600	40°02' N	13°32' E
082	600	40°02' N	13°32' E

TABLE 4

Comparison of amounts (in p. p. b.) of Sc, Rb, Zn, Fe, Co from different authors

	Peeters 080 (600 m)	Robertson (11)	Piper-Goles (6)	Mackensie Goldberg (8)	Goldberg (9)	McDonald (7)
Sc	.010 ± .003	.003	6.3	.04	.04	.04
Rb	96. ± 19.	—	105.	120.	120.	120.
Zn	150. ± 29.	2.	13.	10.	10.	10.
Fe	37. ± 13.	30.	23.	10.	10.	10.
Co	.19 ± .05	.008	.44	.50	.10	.10



CAMPAGNE INTERNATIONALE en Mer TYRRHENIENNE
Participation Belge
Gek & Temp. de Surface
Carte I

NOTE : Les pacours E_1, E_2, E_3, E_4, effectués dans cette région ont été reportés sur la carte II.

Fig. 1. — Route of the different ships participating at the measurements of surface currents and temperature

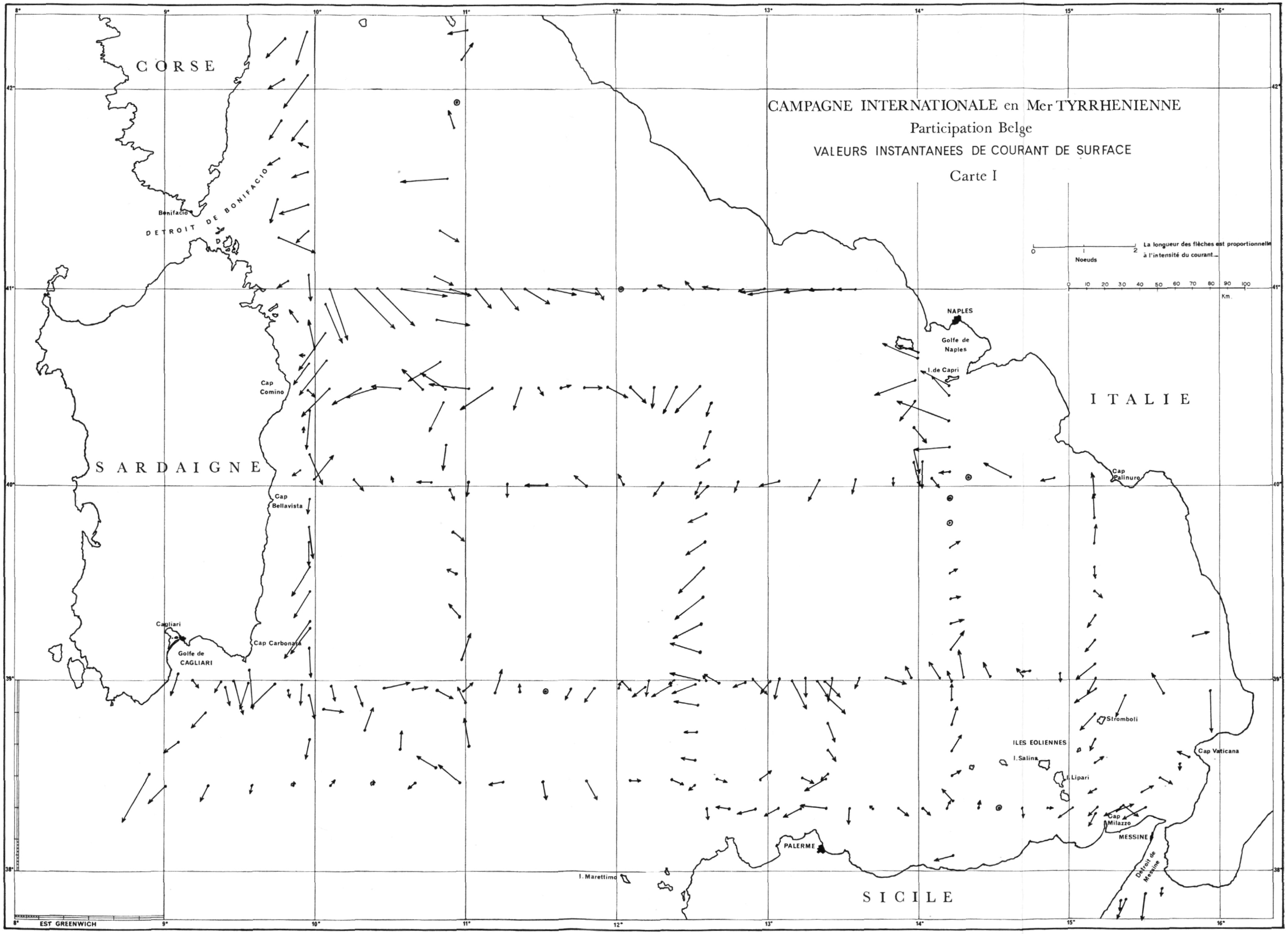


Fig. 2. — Instantaneous values of surface currents in the Tyrrhenian Sea.

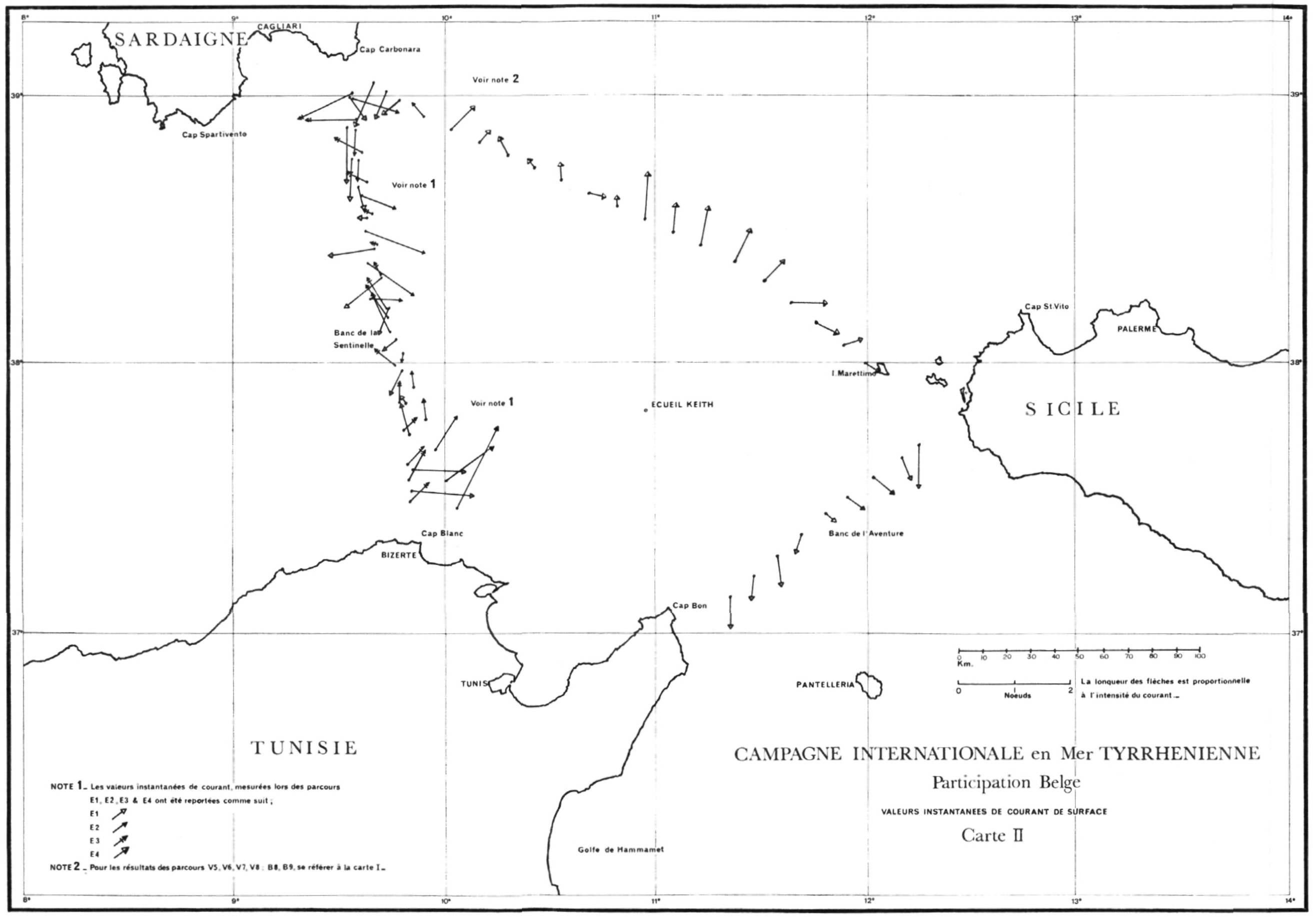
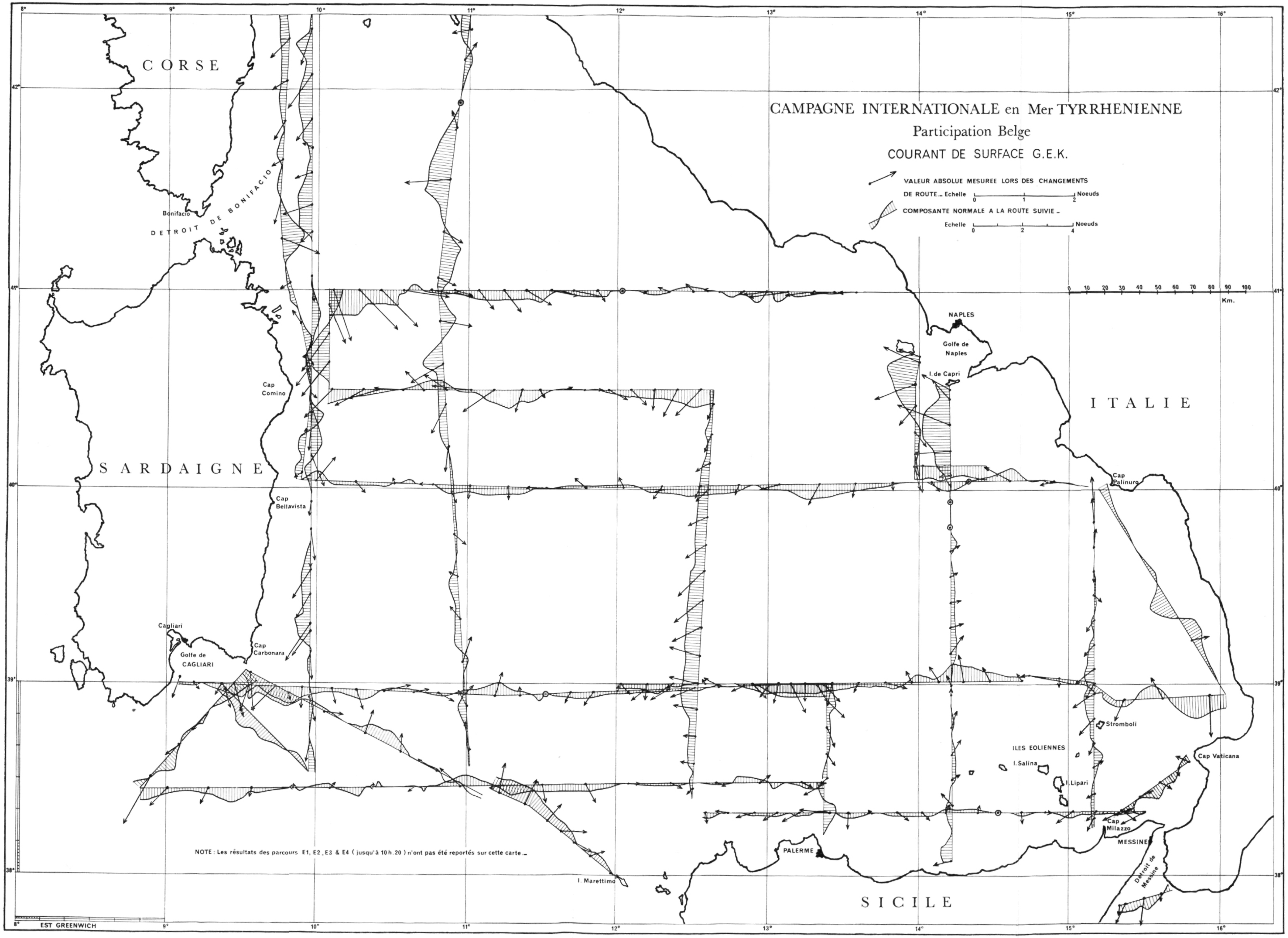


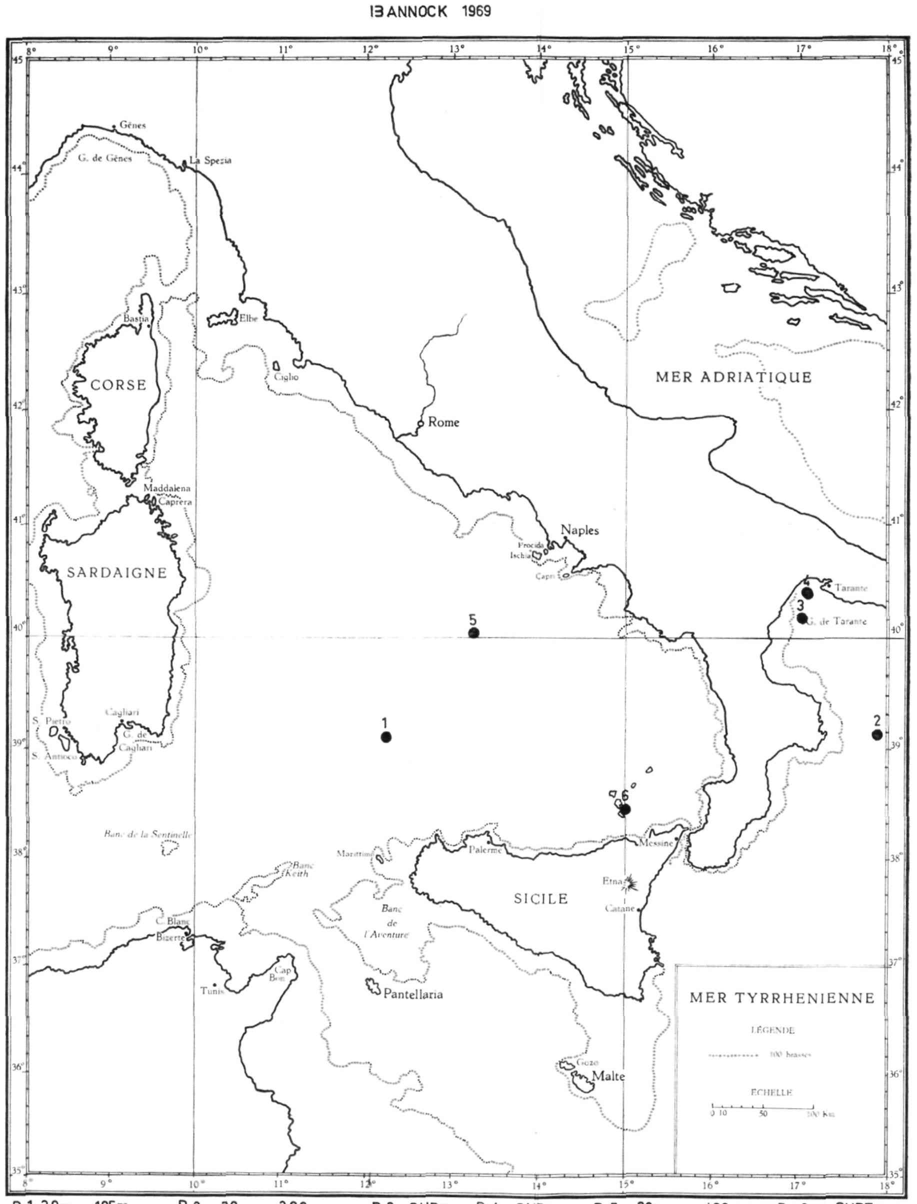
Fig. 3. — Instantaneous values of surface currents in the straits between Sicily, Tunis and Italy



CAMPAGNE INTERNATIONALE en Mer TYRRHENIENNE
Participation Belge
COURANT DE SURFACE G.E.K.

NOTE : Les résultats des parcours E1, E2, E3 & E4 (jusqu'à 10 h. 20) n'ont pas été reportés sur cette carte _

Fig. 4. — Surface currents in the Tyrrhenian basin.



P.1	20m 40m 95m 135m 145m	195m 395m? 595m 795m 965m
P.2	20m 50m 100m 150m	200m 400m 600m 800m 1000m
P.3	SURF.	
P.4	SURF.	
P.5	20m 50m 100m 150m 200m	400m 600m
P.6	SURF.	

Fig. 5. — Position of the Stations

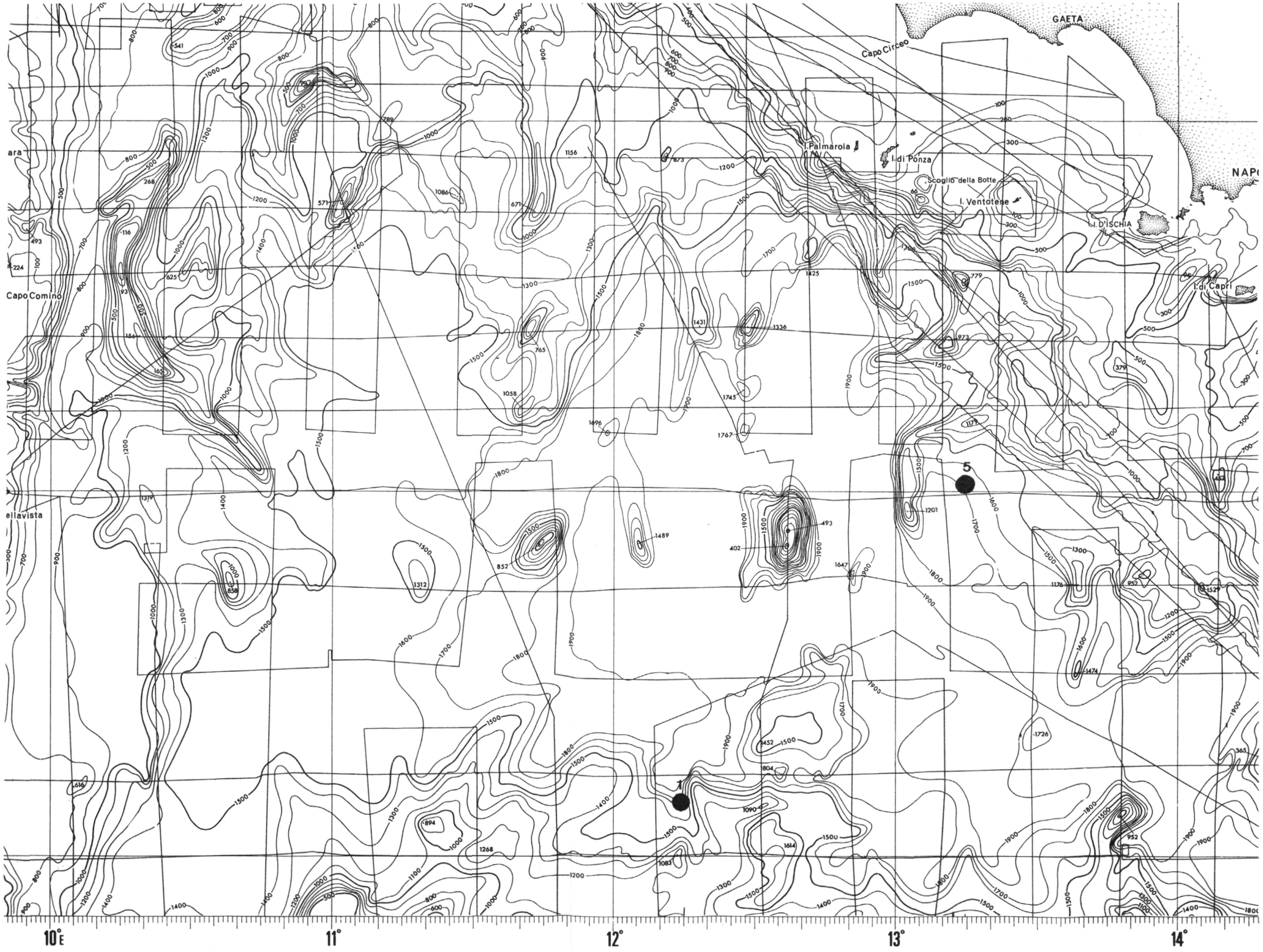


Fig. 6. — Position of the stations plotted on the maps of Dr. ALLAN and Prof. MORELLI.

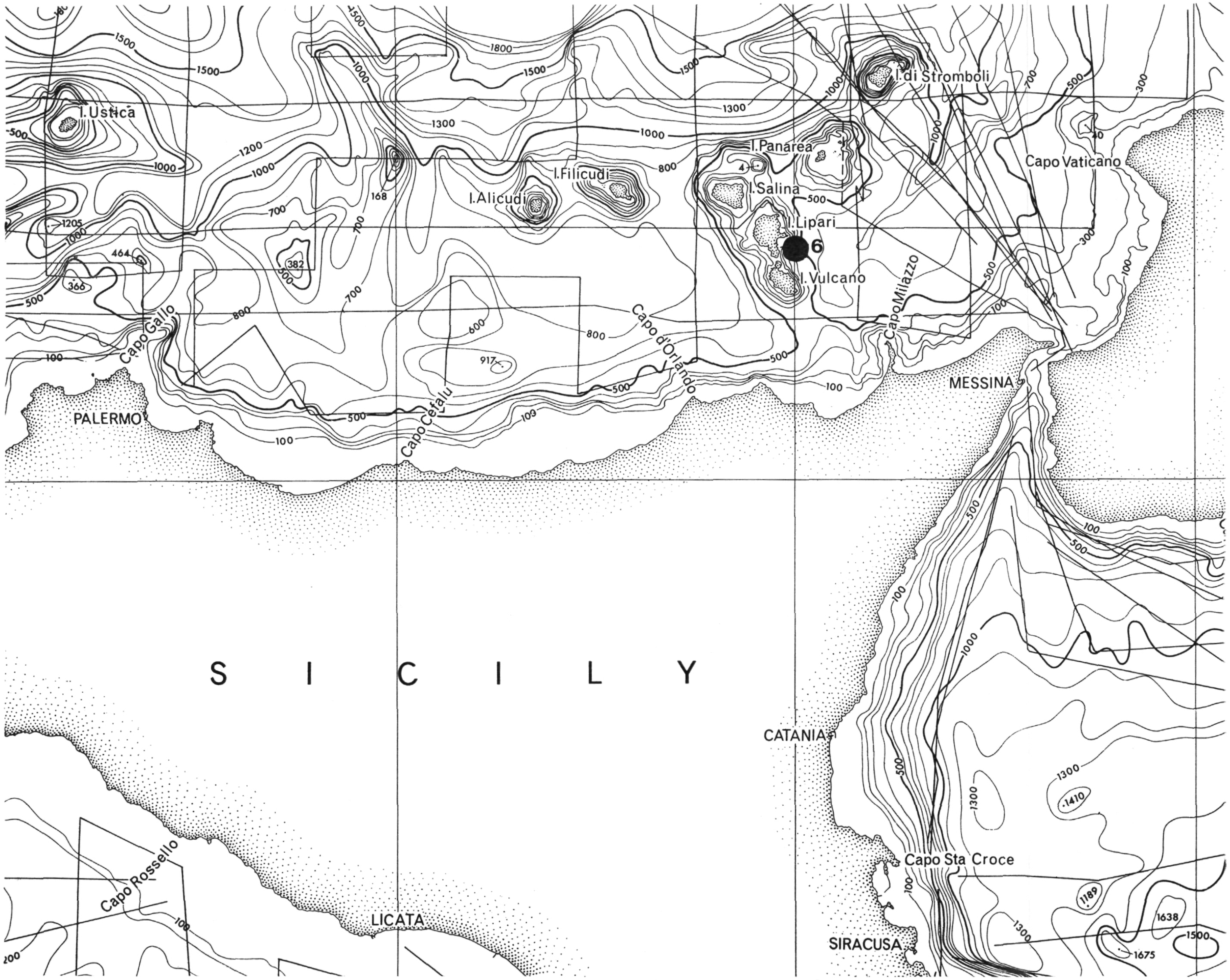


Fig. 7. — Position of the stations plotted on the maps of Dr. ALLAN and Prof. MORELLI

The figures 5 shows the position of the different stations.

The figures 6 and 7 point out the position of the stations indicated on the maps by Dr ALLAN and Prof. MORELLI. These maps show the isobaths of this basin.

The figures 8, 9 and 10 show the spectra of sea water samples at 100 m and 600 m depth taken one and two months after the irradiation respectively.

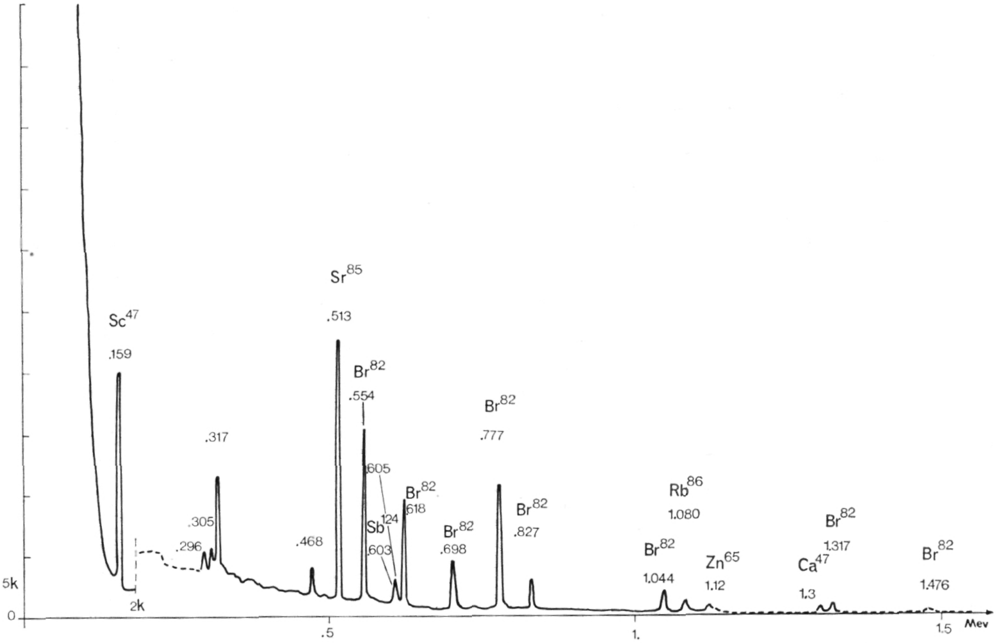


Fig. 8. — Spectrum of sea-water sample (at 100 m depth) one month after irradiation
irradiation date : 22.01.70
duration of the irradiation : 5 days
date of the measurement : 19.02.70
counting time : 20 minutes
water depth : 100 m

IV. CONCLUSIONS

Generally, our results are comparable with those published by different laboratories (Table 4).

The quantitative analysis can be improved and we hope to get less than 10 % errors.

Anyway, from these results, we can conclude that the neutronic activation analysis is a valid method for quantitative analysis but we have to think of a possible contamination, in this case, by Zn.

On the other hand, we observe constant variation of Sc, Fe, Co, Zn due probably to the volcanic amounts.

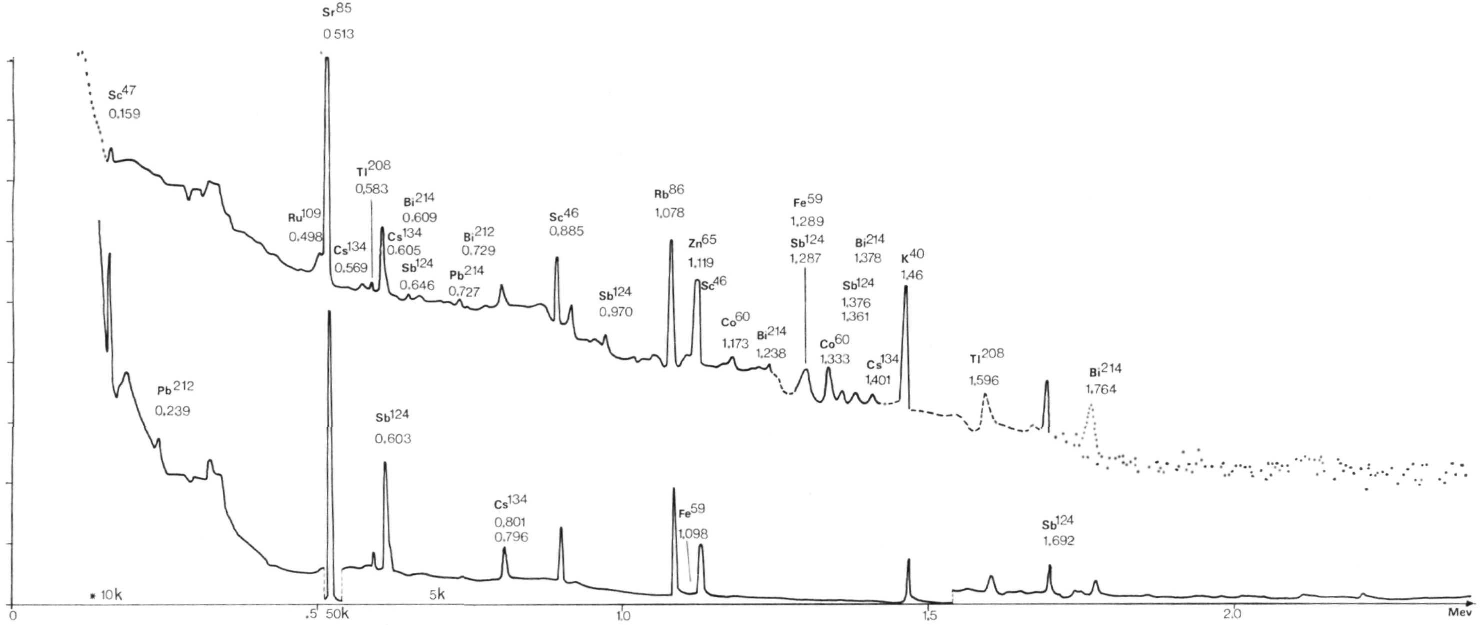


Fig. 9. — Spectrum of sea-water sample (at 100 m depth) two months after irradiation

irradiation date : 22.01.70
duration of the irradiation : 5 days
date of the measurement : 17.03.70
counting time : 1000 minutes
* full scale counts K = 1000 counts/channel
water depth : 100 m

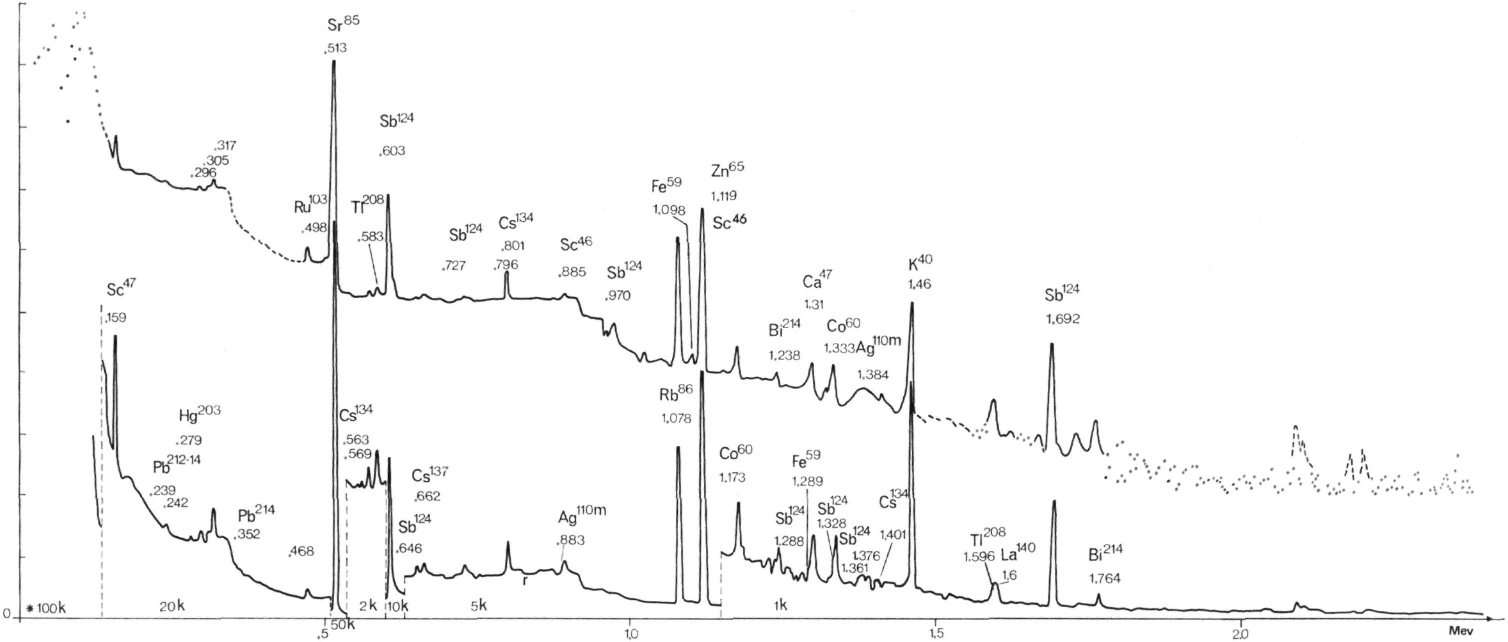


Fig. 10. — Spectrum of sea-water sample (at 600 m depth) two months after irradiation

irradiation date : 22.01.70
duration of the irradiation : 5 days
date of the measurement : 12.03.70
counting time : 1000 minutes
* full scale counts K = 1000 counts/channel
water depth : 600 m

We estimate that it is too early to draw a real conclusion from so few results.

Indeed the reactor of Saclay was in poverty for a long time and we were obliged to try an irradiation at Peten (Holland) but this irradiation does not work for many contaminations due to the reactor itself.

At last none comparison is possible between sampling at different depths of the Tyrrhenian Sea and sampling at the same depths into the Gulf of Tarente because we do not yet get results of the last analysis.

This comparison will be the object of an other publication.

V. ACKNOWLEDGEMENTS

We will express our thanks to Professor A. CAPART, Chairman of the NATO Subcommittee on Oceanographic Research, who, by its energy and its will, was helpful to the realization of many oceanographic expeditions up to the oriental coasts of Turkey. His oceanographic experience and knowledge have been a precious assistance for our investigation.

We are deeply indebted to Professor MORELLI and Professor LACOMBE for their help to the realization of these expeditions.

At last, we are grateful to the technic and scientific staff of the Physical Oceanography Laboratory at the Institut royal des Sciences naturelles de Belgique for their assistance to bring our first study to a successful issue.

INDEX BIBLIOGRAPHIQUE

ANICHINI, C.

1967. *Contribution à la connaissance des courants de la Méditerranée.* (NATO, Technical Report 42, Sept. 1967. Sub-Committee on Oceanographic Research.)

1969. *Projet Mer Tyrrhénienne* (Technical Report 44, janvier 1969.)

ALLAN, T. D. and MORELLI, C.

1970. *Charts of the bathymetry contour interval 100 fathoms soudings connected according to Matthew's tables.* (May 1970. Stempata e cura dell Istituto Idrografico delle Marine, Genova.)

PEETERS, E. and LACROIX, R.

1968. *International Symposium on the application of neutron activation analysis in oceanography* (NATO Sub-Committee on Oceanographic Research, pp. 103-115, June 1968.)

CAPART, A. and PEETERS, E.

Technical Report 51 (under Press). (Sub-Committee on Oceanographic Research of NATO.)

PIPER, D. R. and GOLES, G. E.

1969. *Analytica Chimica Acta.* (Vol. 47, 3 560.)

MC DONALD, G. D. F.

1959. *Researches in Geochemistry.* (Edited by Abelson, P. H. Wiley, New York.)

GOLDBERG, E. D.

1963. *The Sea.* (Vol. 2, p. 3, M. N. Hill ed., Intersience London.)

1965. *Chemical oceanography.* (p. 163, J. P. Riley and G. Shirrow eds., Academic Press, New York and London.)

SCHUTZ, D. F. and TUREKIAN, K. K.
1965. Geochim. cosmochim. Acta 29, 259.

ROBERTSON, D. E.
1968. *International Symposium on the application of neutron activation analysis in oceanography*. (NATO Sub-Committee on Oceanographic Research, pp. 143-212, June 1968.)